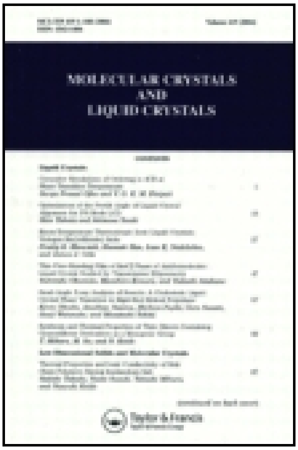

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FABRICATION OF ORIENTATION-CONTROLLED MEROCYANINE J-AGGREGATES FROM VAPOR PHASE

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FABRICATION OF ORIENTATION-CONTROLLED MEROCYANINE J-AGGREGATES FROM VAPOR PHASE

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The absorption spectrum of merocyanine (BTET) film deposited on a NaCl substrate showed a broad absorption band in the wavelength region between 450 nm and 550 nm and a narrow peak at 640 nm. The former bands were assigned to the absorption bands of α- and β-form crystal, the latter peak was assigned to J-band. BTET film was composed of square-shaped and rectangular crystals grown epitaxially. The square-shaped crystal was composed of α-form and the rectangular crystal was composed of α-form and J-aggregate. The formation mechanism of J-aggregate in film was discussed.

Keywords: J-aggregate; merocyanine; vapor deposition

1. INTRODUCTION

Recently, self-organizing organic dyes have played crucial roles in viewpoints of both fundamental science and technological applications. Among them, J-aggregate has attracted much attention because of large optical non-linearity and ultra-fast response time for nonlinear optical materials. J-aggregate is characterized by sharp absorption band (J-band) red-shifted from that of isolated molecules.

There have been many reports on formation and characterization of J-aggregates in Langmuir-Blodgett film but few reports on those in vapor-deposited film. We have investigated previously the J-aggregate formation in merocyanine film prepared by vapor deposition method. An amorphous merocyanine film formed J-aggregate after exposure to dimethyl amine aqueous vapor and/or soaking into aqueous solution containing various metallic salts [1,2].

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In this work, we tried direct preparation of J-aggregate film of merocyanine dye from vapor phase by selecting the evaporation conditions.

2. EXPERIMENTAL

3-Ethyl-5-[2-(3-ethyl-2-(3H)-benzothiazolylidene)-ethylidene]-2-thioxo-4-thiazolidinone (BTET) was used here as merocyanine dye. Figure 1 shows the molecular structure of BTET. The BTET was vapor-deposited onto a glass plate and a cleaved surface of NaCl single crystal kept at 20°C and 80°C from a fused silica glass crucible in a vacuum of 10^{-3} Pa. The deposition rate was controlled about 0.2 nm/min and 2 nm/min. The thickness of the BTET films was about 30 nm. The structure and absorption characters of the films were investigated by transmission electron microscopy (TEM) and visible absorption spectroscopy.

3. RESULTS AND DISCUSSION

Figure 2 shows the absorption spectra of the BTET films vapor-deposited on a glass plate and a NaCl substrate. According to Chang *et al.* BTET has two crystal structures; α-form (triclinic; $a = 0.7458$, $b = 1.0736$, $c = 1.1039$ nm, $\alpha = 95.16°$, $\beta = 107.68°$, $\gamma = 103.09°$) and β-form (monoclinic; $a = 1.1650$, $b = 0.9026$, $c = 1.5654$ nm, $\beta = 92.24°$). Each crystal has the absorption peak at 480 nm and 508 nm, respectively [3]. The absorption spectrum of BTET film deposited on a glass plate kept at 20°C with the deposition rate of 2 nm/min shows a broad absorption band in the wavelength region between 450 nm and 550 nm, as shown in Figure 2(a). This is a superposition of absorption spectra of α- and β-form crystals. On the other hand, the absorption spectrum of the BTET film deposited on a NaCl substrate with same deposition conditions shows a similar broad absorption band and an absorption peak at 574 nm, as shown in Figure 2(b). Tanabe *et al.* reported that BTET forms J-aggregate on a (001) surface of AgBr crystal and J-band appears at 575 nm [4]. Therefore, the absorption peak at

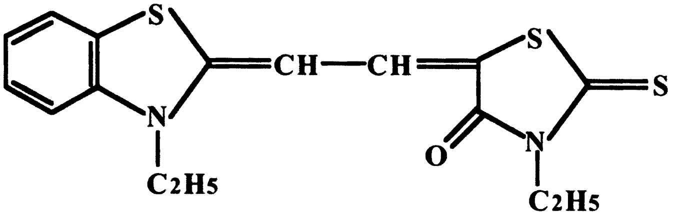

FIGURE 1 Molecular structure of merocyanine dye (BTET).

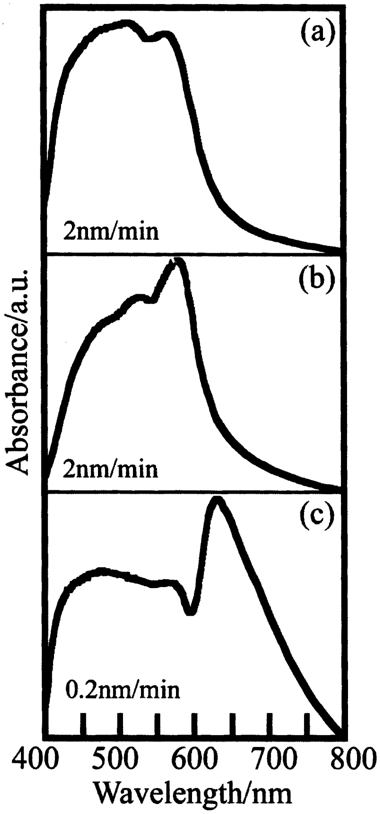

FIGURE 2 Absorption spectra of the BTET films deposited on a glass plate at 20°C (a) and a NaCl substrate at 20°C (b) and 80°C (c) with various deposition rates.

574 nm was assigned to J-band. When BTET was deposited on the NaCl substrate kept at 80°C with the deposition rate of 0.2 nm/min, the intense absorption peak appears at 640 nm on the red side of the broad absorption band, as shown in Figure 2(c). This absorption peak was also assigned to J-band. The red-shift of J-band to longer wavelength may be attributed to the increase of the number of molecules in J-aggregate and/or J-aggregate orientation on the substrate. These findings indicate that the BTET film forms J-aggregate on the NaCl substrate and the structure of J-aggregate heavily depends on the deposition condition.

Figures 3(a) and (b) show TEM images and the electron diffraction patterns of the BTET films deposited on a glass plate and a NaCl substrate kept at 20°C with the deposition rate of 2 nm/min. The BTET film deposited on a glass plate was composed of small crystals with various shapes.

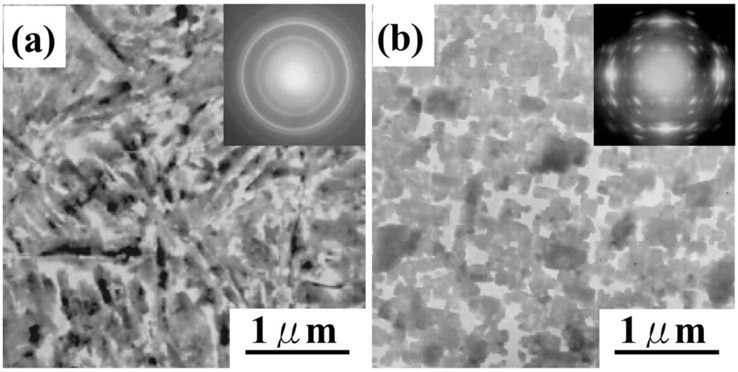

FIGURE 3 TEM images and electron diffraction patterns of BTET films deposited on a glass plate (a) and a NaCl substrate (b) at 20°C with the deposition rate of 2 nm/min.

The electron diffraction pattern of the film shows the ring pattern. Most of the reflection rings can be accounted by using the unit cell parameters of the α-form crystal. However, the reflection rings corresponding to β-form crystal cannot be observed clearly. Therefore, BTET deposited on the glass plate seems to crystallize in α-form predominantly. On the other hand, BTET film deposited on a NaCl substrate was composed of plate-like crystals with 0.1–0.5 μm in size. The electron diffraction pattern of the film showed the two sets of single net pattern with the reflection spots corresponding to the interplanar distance of 1.36 nm and 1.30 nm, and those of 0.82 nm and 0.69 nm crossing orthogonally. On comparison of the observed spacings and the calculated ones, these patterns corresponded to the single net patterns of 001 and 010, and $0\bar{1}1$ and $1\bar{0}1$ of the α-form crystal and their higher order reflections, respectively. The plate-like crystals grew epitaxially on the NaCl substrate. Careful observation of the diffraction pattern reveals the extra spots which cannot index using the unit cell parameters of the α- and β-form crystal. These spots seem to be assigned to the reflection spots from the J-aggregate crystals because the J-band appears in the absorption spectrum of the film. These crystals are too small to investigate the structure of J-aggregate crystal. Further structural analysis was carried out for the film deposited on the NaCl substrate kept at 80°C with the deposition rate of 0.2 nm/min. The BTET crystals grew larger under this evaporation condition, as shown in Figure 4 The BTET film was composed of almost square-shaped crystals with 1 μm × 1 μm and rectangular crystals with several μm × 1 μm. The edges of both crystals aligned to the [110] or [$\bar{1}$10] directions of the substrate crystal. The electron diffraction pattern of the square-shaped crystal shows

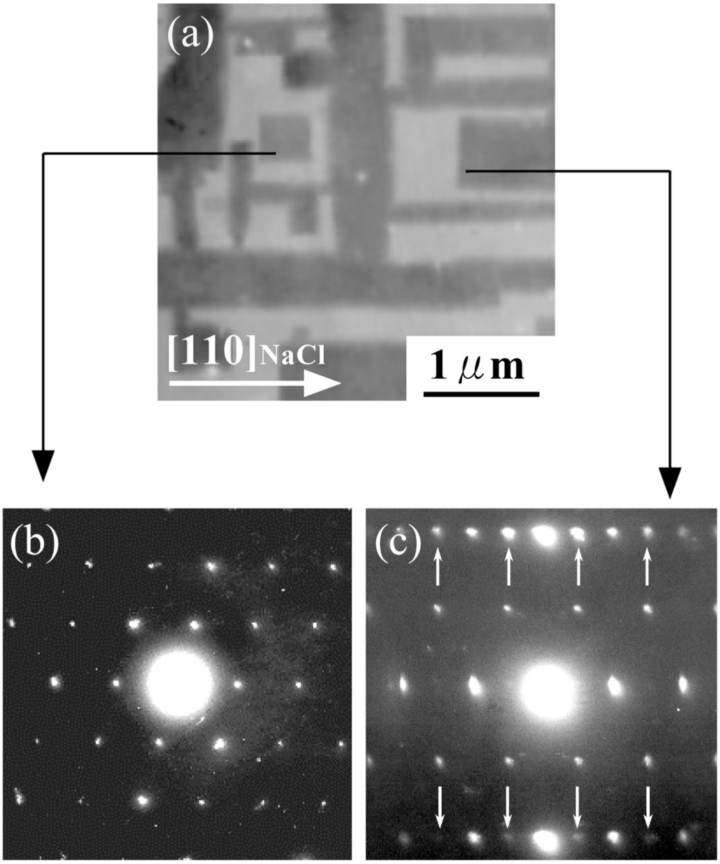

FIGURE 4 TEM image (a) of BTET film deposited on a NaCl substrate at 80°C with the deposition rate of 0.2 nm/min and electron diffraction patterns obtained from the square-shaped (b) and the rectangular crystals (c).

the single net pattern with 001 and 010 reflection spots of the α-form crystal. On the other hand, the electron diffraction pattern of the rectangular crystal shows the single net pattern with $0\bar{1}0$ and $10\bar{1}$ reflection spots of the α-form crystal. However extra spots indicated by arrows also appears in the diffraction pattern. These spots may be originated from the J-aggregate crystal. Therefore the rectangular crystal is composed of α-form crystal and the J-aggregate crystal. Figure 5 shows the schematic representation of the electron diffraction patterns. On comparison between the electron diffraction pattern and the crystal morphology, it was found that the direction along the edge of the square-shaped crystal corresponds to the $[0\bar{1}1]$ axis of the α-form crystal. The electron diffraction pattern of

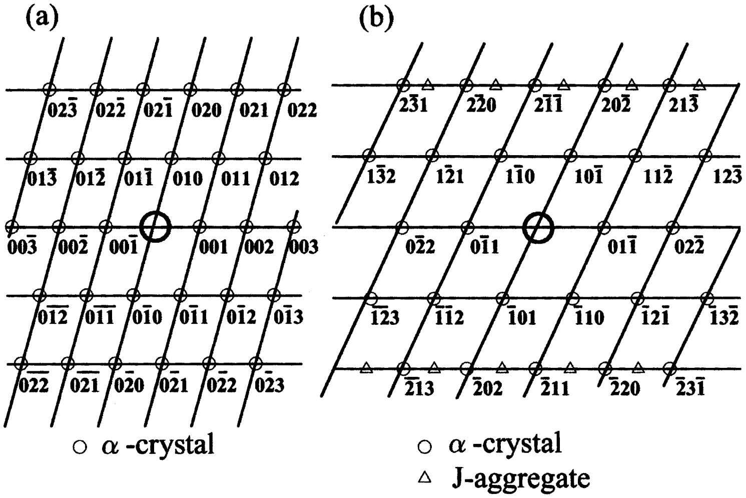

FIGURE 5 Schematic representations of the electron diffraction patterns obtained from the square-shaped (a) and the rectangular crystals (b).

the square-shaped crystal indicates that the $(5\bar{2}\bar{2})$ plane of the α-form crystal oriented parallel to the substrate surface. Consequently, it is concluded that the square-shaped crystals grew with the following epitaxial relation with respect to the substrate NaCl crystal: $(5\bar{2}\bar{2})\ [0\bar{1}1]_{\alpha}$-BTET // (001) $\langle 110\rangle_{\mathrm{NaCl}}$. The normal direction of the longitudinal edge of the rectangular crystal also corresponds to the $[0\bar{1}1]$ axis of the α-form crystal. In this crystal, however, the (155) plane of the crystal oriented parallel to the substrate surface. The rectangular crystals grew with the following epitaxial relation with respect to the NaCl crystal: (155) $[0\bar{1}1]_{\alpha\text{-BTET}}$ // (001) $\langle 110\rangle_{\mathrm{NaCl}}$. The molecular orientation of BTET on the NaCl substrate is represented schematically in Figures 6 and 7. The molecular plane of BTET in the square-shaped crystal oriented almost parallel to the substrate surface, as shown in Figure 6. On the other hand, BTET molecules in the rectangular crystal adsorb in the edge-on state on the (001) NaCl surface, as shown in Figure 7(a). It is well known that molecules in aggregates form columns, or one-dimensional stacks, in which molecules are packed together face-to-face (plane-to-plane) [5]. In order to construct such face-to-face stacks, adjacent molecules must slip against each other along the direction of the long molecular axis of merocyanine, as shown in Figure 7(b). Tanabe *et al.* reported that merocyanine dyes with C=S bond adsorb in the edge-on state on the AgBr surface by the sulfur atom in the thiocarbonyl group in contact with a silver atom of the AgBr surface [4]. In

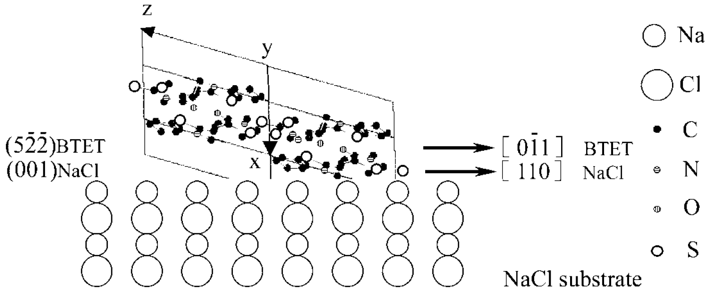

FIGURE 6 Schematic representation of the molecular orientation of BTET in the square-shaped crystal on a NaCl substrate.

the case of BTET, molecules adsorbed on the NaCl surface interact strongly between S atom of C=S bond and Na atom of the uppermost NaCl surface. This leads to molecular slip and formation of J-aggregate.

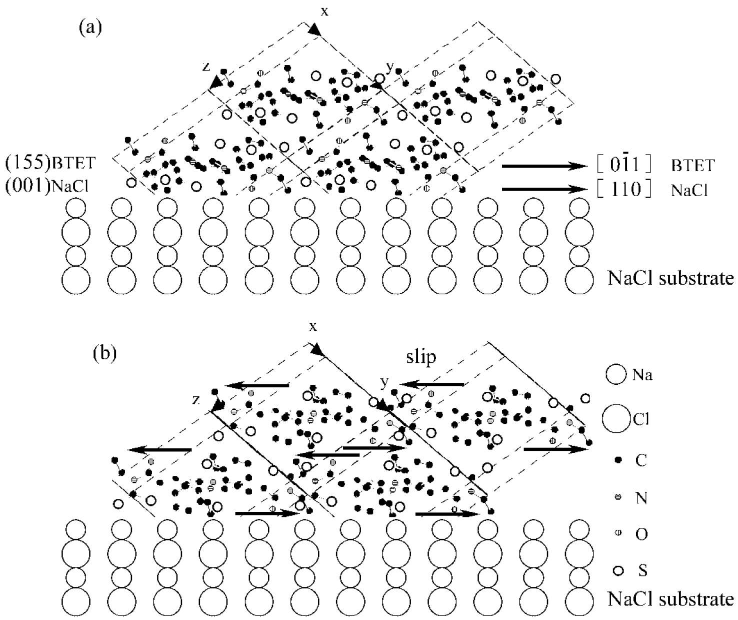

FIGURE 7 Schematic representations of the molecular orientations of BTET in the α-form (a) and J-aggregate (b) crystals on a NaCl substrate. Arrows indicate the slipping direction of BTET molecules in J-aggregate crystal.

CONCLUSION

Thin film of J-aggregate of merocyanine (BTET) was directly prepared from vapor phase. The formation of J-aggregate heavily depends on the deposition condition. BTET film on a NaCl substrate was composed of square-shaped and rectangular crystals grown epitaxially. The square-shaped crystal was composed of α-form crystal and the rectangular crystal was composed of α-form and J-aggregate crystals. The epitaxial relation of J-aggregate crystal was $(155)\ [0\bar{1}1]_{\text{J-BTET}} \,//\, (001)\ \langle 110 \rangle_{\text{NaCl}}$. The formation of J-aggregate seems to be caused by slipping by the interaction between BTET molecule and NaCl substrate.

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