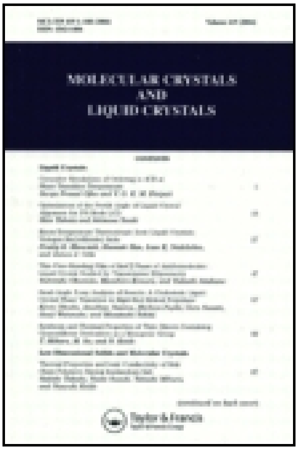

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Characterization of Quinacridone Derivative in Thin Film

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Characterization of Quinacridone Derivative in Thin Film

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2,9-Dimethyl quinacridone (QD-Me) grew epitaxially on a KBr substrate took two kinds of molecular orientations. The absorption property of QD-Me film depended on the molecular orientation. When QD-Me molecules oriented parallel to the substrate surface, the intermolecular charge transfer was contributed effectively to the absorption intensity in the short wavelength region.

Keywords: quinacridone derivatives; epitaxy; VIS spectroscopy; TEM; AFM

INTRODUCTION

Thin films of quinacridone(QD) compounds have been extensively studied as functional materials, because of their excellent fastness properties as well as pronounced photovoltaic and photoconductive activities. The application potential of organic films is heavily depended on the molecular arrangement[1-3]. However, the relation between the molecular arrangement and photoelectronic properties is not so clear.

In this study, we prepared the epitaxial films of 2,9-dimethyl quinacridone (QD-Me). The morphology and structure were investigated by TEM and AFM and their optical properties were discussed based on the molecular arrangement.

EXPERIMENTAL

QD-Me was deposited on an air-cleaved (001) surface of KBr in a vacuum of 10^{-3}Pa. The thickness of the films was controlled to about 20nm. The absorption spectra of the films were measured by using a Shimadzu UV-2200 spectrometer.

RESULTS AND DISCUSSION

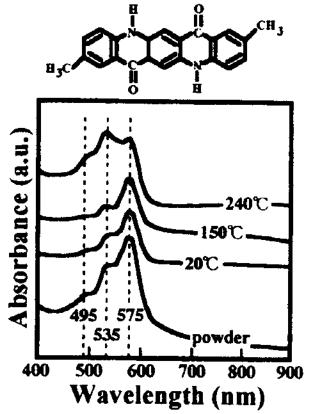

FIGURE 1 VIS spectra of the original QD-Me powder and the films deposited at various temperatures.

The VIS spectra of the original QD-Me powder and the films deposited on the KBr substrates kept at 20 and 150℃ showed an absorption peak at 575nm and two shoulders around 535nm and 495nm. In the case of the film deposited at 240℃, on the other hand, the absorption intensity around 535nm was remarkably strong and appeared as peak, as shown in Fig. 1. Rossi et al have reported the photophysical properties of linear-trans-QD[4]. The prominent peak at long wavelength region and a shoulder at short wavelength region were assigned to the zero-phonon S_0-S_1 transition and C-C stretching vibrations which were resulted from excimeric or charge transfer (CT) between molecules, respectively. From the similarity in molecular structure between QD and QD-Me, we concluded that the absorption bands at 575nm and in the wavelength region of 480-550nm could be assigned to the zero-phonon transition and skeletal vibrations, respectively. Since no differences in the positions of X-ray diffraction patterns between the original powder and every film were observed, it is clear that QD-Me has the same crystal structure in powder and film. Therefore, change in absorption intensity around 535nm seems to be caused by the molecular orientation in the film depending on the substrate temperature.

The QD-Me film deposited at 20℃ was consisted of small needle-like crystallites crossing orthogonally. Their long axes ran along the <100> direction of the substrate crystal. The size of these crystallites became larger with increasing temperature of the substrate. Figure 2 shows the electron micrographs and electron diffraction (ED) patterns of the QD-Me films deposited at 150 and 240℃. The films were composed of rod-like or plate-like crystals. The ED patterns from the films deposited at 20 and 150℃ gave the same fiber pattern whose fiber period was 0.66nm . However, the ED pattern of the film deposited at 240℃ displayed a single net pattern, with the diffraction spots corresponding to the lattice spacings of 1.62nm and 0.63nm crossing at 108° . When the film deposited at 150℃ was tilted against the incident beam at about 38° around the [100] direction of the KBr substrate crystal, the single net pattern was observed. This pattern was quite similar to the pattern of the film deposited at 240℃. Consequently, QD-Me took two kinds of orientations on the KBr substrate.

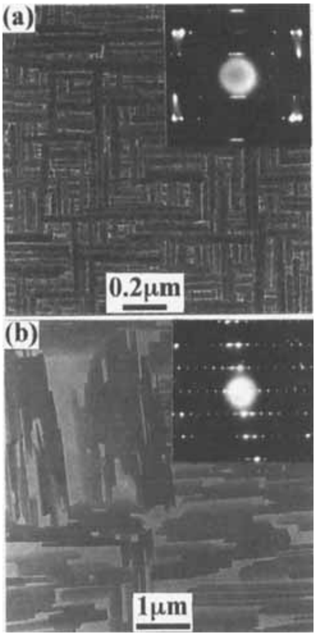

FIGURE 2 TEM images and ED patterns of QD-Me films deposited at 150℃ (a) and 240℃ (b).

The high-resolution AFM images of the rod-like and plate-like crystals showed the lattice fringes and many stripes were observed in the fringes, as shown in Fig.3. The length and width of each ellipse obtained from the plate-like crystal were 1.62nm and

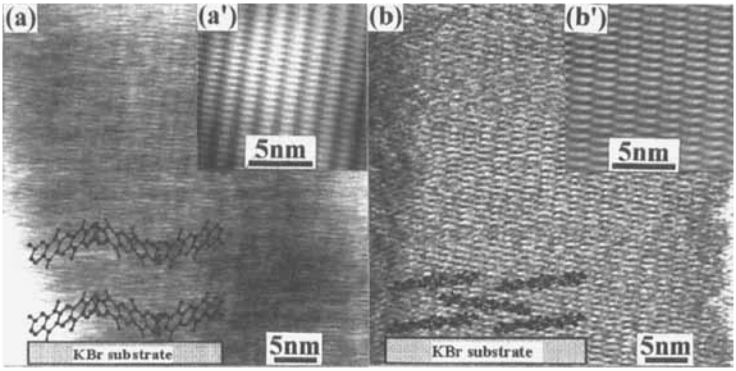

FIGURE 3 AFM images before and after FFT filtering and molecular orientations of QD-Me films deposited at 150℃ (a, a') and 240℃ (b, b') .

0.63nm, respectively. These values were in good agreement with those of calculated molecular size of QD-Me. Therefore, we concluded that each ellipse was consisted of the individual QD-Me molecule. The molecules were orientated parallel to the substrate as inserted in figure. On the other hand, the size of each stripe obtained from the rod-like crystal was 1.60nm x 0.53nm in length and width, which coincided with the molecular size projected along the direction making an angle of about 55° against the normal of molecular plane. The long axes of QD-Me molecules deposited at 150°C oriented parallel to the surface of substrate, but the short axes stood obliquely at about 55° as illustrated in figure.

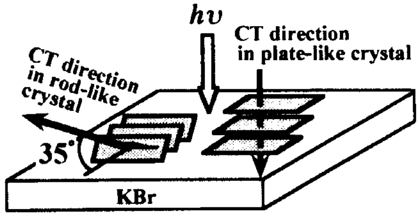

FIGURE 4 CT directions in rod-like and plate-like crystals.

It is well known that the most effective intermolecular CT between planar molecules stacked cofacially occurs along the direction of normal to the molecular plane. In the epitaxial film prepared at 240℃, the direction of intermolecular CT is normal to the substrate surface, but is inclined at 35° in the film below 150℃, as shown in Fig.4. Therefore, it is concluded that the high intensity of absorption peak at 535nm of the film at 240℃ is attributed to the effective intermolecular CT.

Acknowledgments

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