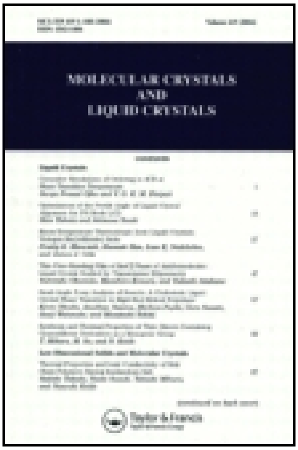

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Structures of Perylene Derivatives in Thin Film

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Structures of Perylene Derivatives in Thin Film

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Three perylene compounds (H-PTC, Me-PTC and $PhMe_2$-PTC) were grown epitaxially on a cleaved surface of a KBr crystal. The structure and molecular orientations in the film were investigated by transmission electron microscopy (TEM) and AFM observations. The combination of TEM and AFM techniques was powerful method to detect the molecular orientation in a thin film.

Keywords: perylene derivatives, epitaxy, TEM, AFM

INTRODUCTION

Thin films of perylene compounds have recently attracted a great deal of attention as functional materials because of their high photoconductivity and n-type character which is rare in organic compounds. Application potential of organic films heavily depends on the controllability of the molecular orientation. We have studied the relationship between physical properties and molecular orientation in the film. The photovoltaic and/or nonlinear optical properties of epitaxial films were enhanced by the control of molecular orientation[1-3].

In this study, three perylene derivatives were vapor-deposited on a KBr (001) surface. The structures and molecular orientations in the film were investigated by the transmission electron microscope (TEM) and atomic force microscope (AFM).

EXPERIMENTAL

Perylene derivatives used here were perylene-3,4:9,10-biscarboxylic diimide (H-PTC), N,N'-dimethylperylene-3,4:9,10-bis (dicarboximide) (Me-PTC) and N,N'-bis (3,5-xylyl) perylene-3,4:9,10-bis (dicarboximide) ($PhMe_2$-PTC). Molecular structures are shown in Figure 1. Three perylene compounds were vapor-deposited on an air-cleaved (001) surface of KBr from a fused silica crucible heated by a tungsten coil. The deposition rate was controlled to about 2 nm/min in thickness monitored by a quartz crystal microbalance. Morphology and molecular orientation of thin film were observed by TEM (JEM-2010 (JEOL), H-7100 (Hitachi)) and AFM (SPA300 (Seiko)).

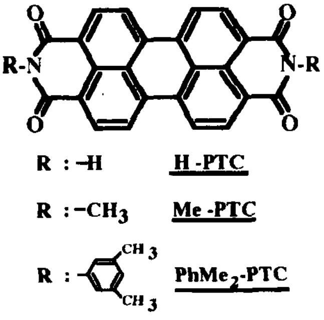

FIGURE 1 Molecular structures of perylene derivatives.

RESULTS AND DISCUSSION

Figure 2 shows the electron micrographs of Me-PTC films deposited on a KBr substrate kept at various temperature. The film deposited on the substrate kept at 20°C consisted of a continuous film of crystallites of about 100nm in size. On the other hand, Me-PTC deposited on the substrate kept at 100°C and 150°C forms well oriented rectangular crystals and trapezoid crystals. The structure and molecular orientation of Me-PTC film were described in detail elsewhere[4]. The Me-PTC crystals deposited on a KBr substrate showed three types of orientations with respect to the substrate crystal:

(a) $[010](10\bar{1})_{Me\text{-}PTC}//[110](001)_{KBr}$,

(b) $[010](001)_{Me\text{-}PTC}//[110](001)_{KBr}$,

(c) $(102)_{Me\text{-}PTC}//(001)_{KBr}$ and $[010]_{Me\text{-}PTC}\angle[110]_{KBr}=\pm 15°$.

At 20°C, all three orientations were observed and type (a) orientation was predominant. At 100°C Me-PTC grew epitaxially in type (b) orientation in

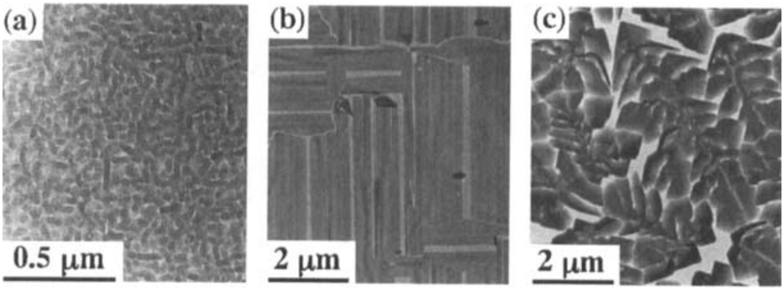

FIGURE 2 Transmission electron micrographs of Me-PTC films deposited onto a KBr (001) surface held at a temperature of 20°C(a), 100°C(b) and 150°C(c).

which Me-PTC molecules adsorbed obliquely at about 70° to the substrate surface. At 150°C, on the other hand, Me-PTC grew epitaxially in type (c) orientation in which Me-PTC molecules lay parallel to the substrate surface. An enlarged electron micrograph of Me-PTC film with type (b) orientation showed lattice fringes with 1.55nm spacing, corresponding to (010) planes of the Me-PTC crystal. And then, many stripes were observed in the fringes and piled up in the columns with the interval of 0.38nm which corresponds to (100) planes, as shown in Figure 3. An AFM image of same film showed lattice fringes with 1.56 and 0.39nm spacings as shown in Figure 4. This is a good agreement with the electron micrograph shown in Figure 4. According

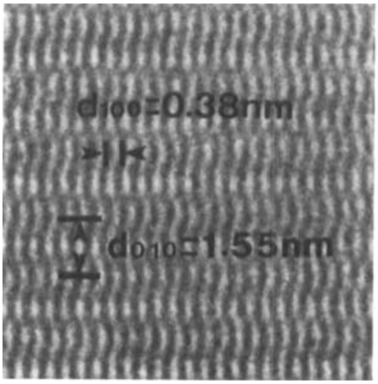

FIGURE 3 Enlarged electron micrograph of the Me-PTC film.

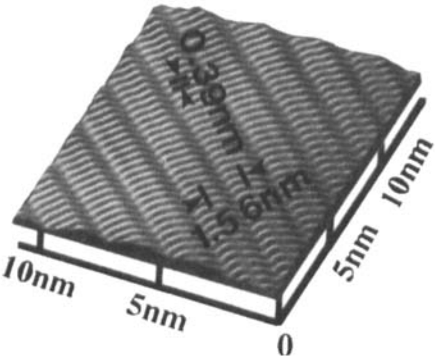

FIGURE 4 AFM image of the Me-PTC film.

to individual stripes corresponded to Me-PTC molecules, the analysis of AFM image makes it possible to elucidate the molecular orientation of perylene at a molecular level.

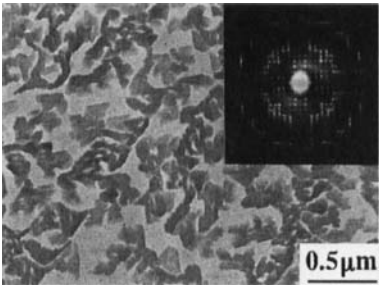

FIGURE 5 Electron micrograph and diffraction pattern of the H-PTC film.

Figure 5 shows the electron micrograph and electron diffraction pattern of H-PTC film deposited at 150°C. The edges of flaky crystallites ran along the [110] direction of the substrate crystal. The electron diffraction pattern of the film showed a superposition of single pattern rotated at 90° with respect to each other. A series of spots on the equator correspond to the interplanar spacing of 0.75nm^{-1}. The layer lines show the interplanar spacing of 0.30nm^{-1} and extra spots appear on four lines with an equidistance of 1.51nm^{-1} between the layer lines. The crystal structure of H-PTC has not been reported, so that, in order to determine the crystal structure of H-PTC, the film was tilted against the incident beam. When the film was tilted about 30° around the [110] axis of the substrate crystal, the electron diffraction pattern gave the rectangular single net pattern with the diffraction spots corresponding to lattice spacings of 1.55nm^{-1} and 1.41nm^{-1}. The $2\theta/\theta$ X-ray diffraction pattern of the film showed only one reflection peak corresponding to lattice spacing of 0.33nm^{-1}. In a homologous series of perylene crystals, planar molecules lie parallel on the (102) plane and the interplanar distance between the stacked perylene molecules is 0.32-0.33nm[5, 6].

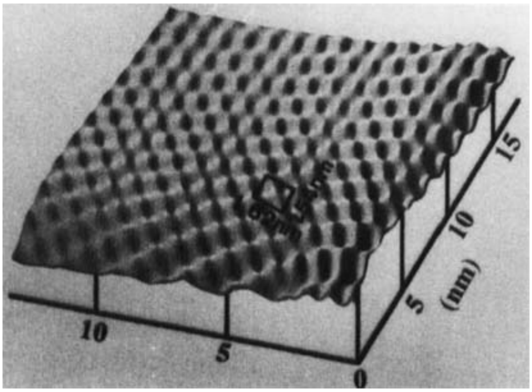

FIGURE 6 AFM image of the H-PTC film.

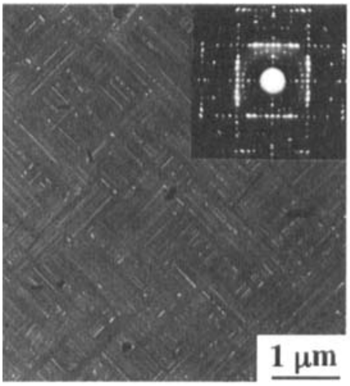

FIGURE 7 Electron micrograph and diffraction pattern of the PhMe2-PTC film.

Therefore, the reflection peak corresponding to lattice spacing of $0.33nm^{-1}$ was assigned to the (102) plane of H-PTC crystal. The H-PTC has the following unit-cell dimensions: a=0.364 nm, b=1.54nm, c=1.41nm and $\beta=93°$. An AFM image of the H-PTC film deposited at 150°C shows ellipses as shown in Figure 6. Each ellipse is assumed to consist of the individual H-PTC molecule. The two-dimensional fast Fourier transformation (2D-FFT) spectrum of the image showed a net pattern with a periodicity of $1.54nm^{-1}$ and $1.62nm^{-1}$. These periodicities are good agreement with the (102) unit mesh which is consisted of the $[010]$ and the $[\bar{2}01]$ axes.

$PhMe_2$-PTC film deposited at 150°C also grew epitaxially. The film was composed of thin plate-shaped crystals crossing orthogonally each other, as shown in Figure 7. Corresponding to such a configuration of the film, the diffraction pattern also has an orthogonal appearance. However, this pattern is a superposition of several single patterns rotated at 90° with respect to each other. The electron diffraction pattern of one crystal showed the single net pattern with the diffraction spots corresponding to lattice spacings of $2.15nm^{-1}$ and $0.37nm^{-1}$. The reflection electron diffraction pattern of the film shows the net pattern with the diffraction spots corresponding to lattice spacings of $0.37nm^{-1}$ and $1.75nm^{-1}$. Figure 8 shows an AFM image of $PhMe_2$-PTC film. Individual

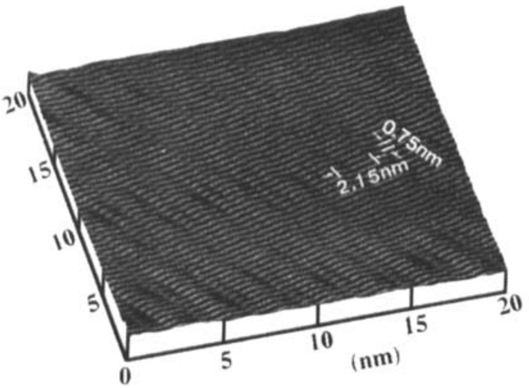

FIGURE 8 AFM image of the PhMe2-PTC film.

$PhMe_2$-PTC molecules can be readily distinguished. The two-dimensional lattice parameters are calculated from the 2D-FFT spectrum of the image, d_{10}=0.75nm and d_{01}=2.15nm.

The molecular orientations of H-PTC and $PhMe_2$-PTC were schematically represented in Figure 9. The H-PTC molecules are piled up parallel to the substrate surface. The $PhMe_2$-PTC molecules, on the other hand, adsorbed obliquely to the substrate surface.

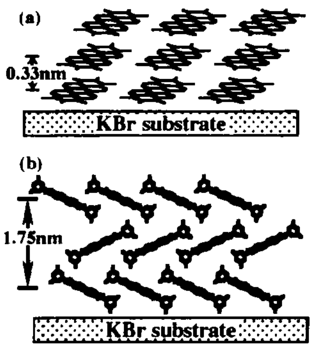

FIGURE 9 Orientations of the H-PTC (a) and PhMe2-PTC (b) molecules.

To conclude, the combination of TEM and AFM techniques is powerful method to detect the molecular orientation in a thin film.

Acknowledgments

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