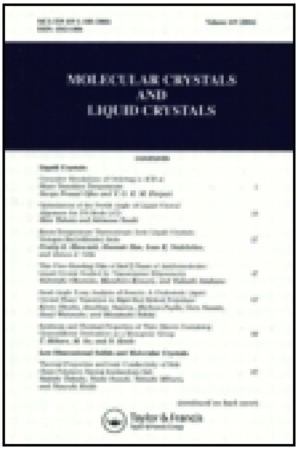

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Effect of Hydrogen-bonding on Crystal Structure of Quinacridone Derivatives in Thin Film

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Effect of Hydrogen-bonding on Crystal Structure of Quinacridone Derivatives in Thin Film

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The different crystal behaviors are found in two quinacridone compounds (QD and QD-Me) films grown epitaxially on an air-cleaved KBr (001) substrate. It is considered to imply the substitution effect on the hydrogen-bonding formation according to the investigation of both absorption properties and crystal structure.

Keywords quinacridones; epitaxy; crystal structure; optical property

INTRODUCTION

In our former report [1], 2,9-dimethyl quinacridone (QD-Me) deposited on an air-cleaved KBr (001) substrate has been studied. It is found that the absorption property of QD-Me film seriously depended on its molecular orientation. The intermolecular hydrogen bonds are believed to be dominant influence on the crystal packing in the multiple crystal modifications exhibited by quinacridone compounds, however, the situation of molecular structural effect on the formation of hydrogen-bonding has not been clear [2-7]. In this study, the linear trans, trans-quinacridone (QD) and its methyl substituent derivative (QD-Me) are investigated and compared to understand the effect of substitution on the formation of hydrogen-bonding, in order to make clear further the correlation of molecular structure and optical properties of the quinacridone derivatives in thin film.

EXPERIMENTAL

Two quinacridone compounds (QD and QD-Me), whose molecular structures are shown in Fig.1, were grown epitaxially on an air-cleaved KBr (001) substrate in a vacuum of 10^{-3}Pa. Their optical properties and crystal structure were investigated with visible and infrared spectroscopy andTEM .

RESULTS AND DISCUSSION

Fig.2 is the visible absorption spectra of QD powder and QD films deposited at different substrate temperatures. Compared with the locations of the absorption peaks of QD powder, those peaks of QD films prepared at various substrate temperature shift to the short wavelength slightly, locating around 490nm, 525nm and 565nm respectively, as shown in Fig.2. It indicates that QD takes different crystal structure in powder and in film. Comparing with the absorption properties of QD-Me [1], QD-Me has the same crystal structure both in powder and films deposited below 150℃. Because in many cases the polymorph in quinacridone compounds is found to be sensitive to the intermolecular hydrogen-bonding [2,5,6], the different crystal behavior between QD and QD-Me films implies the substitution effect on the hydrogen-bonding formation.

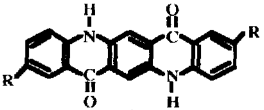

FIGURE 1 Molecular structure of quinacridone derivatives; QD(R=H) and QD-Me(R=CH$_3$).

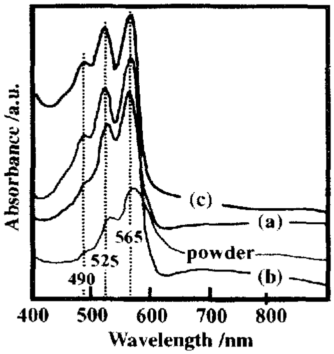

FIGURE 2 Visible absorption spectra of QD powder and QD films deposited at various temperatures; (a) 20℃, (b)100℃ and (c)150℃.

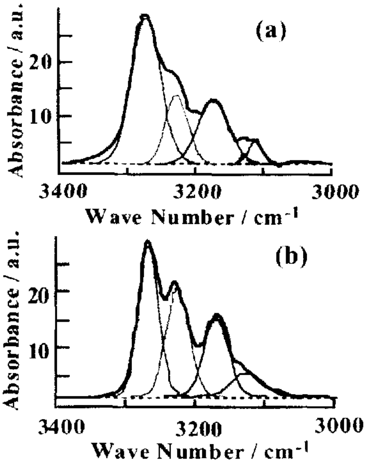

FIGURE 3 FT-IR spectra of QD (a) and QD-Me(b) films in the N-H stretching vibration region.

Figure 3 shows the FT-IR spectra of QD and QD-Me films in the N-H stretching region. The spectra were decomposed to the bands shown with the dotted lines in the figure. The vibration bands from hydrogen bond are observed in the region from 3100cm^{-1} to 3240cm^{-1}, and those from the free N-H appear around 3267cm^{-1}. The degree of hydrogen-bonding (ρ) is calculated as $\rho = I_H/(I_F+I_H)$, where I_H is the absorption intensity of the hydrogen bond of N-H · · O, and I_F is that of the isotropic N-H stretching. In this study, ρ is estimated to be 0.48 for QD films and 0.62 for QD-Me films. The hydrogen-bonding of QD seems to be weaker than that of QD-Me. The molecular adopts a herring-bone packing arrangement with individual stacks of quinacridone molecules rotated with respect to each. Individual molecules are hydrogen bonded through N-H · · O short contacts to four adjacent molecules. That hydrogen-bonding makes the overall stability of the lattice [3-7]. Consequently, we may conclude that in the arrangement of five molecules in crystal unit cell with hydrogen - bonding, the degree of freedom of QD-Me molecule should be modified to satisfy the require- ment to perfect performance of hydrogen bonding, which has been substituted two methyl group in 2- and 9-position. Therefore, the polymorphs exist in QD films, while that was not observed in QD-Me films. This result is coincided with those of TEM and AFM investigation. The typical TEM morphologies and the electron diffraction pattern of QD films are shown in Fig.4. QD films grown epitaxially on KBr substrate show rectangular crystals along the <100> directions of the substrate surface. The crystallinity of films are enhanced with the increasing substrate temperature, however their net electron diffraction patterns are same as shown in Fig.4(c), corresponding to

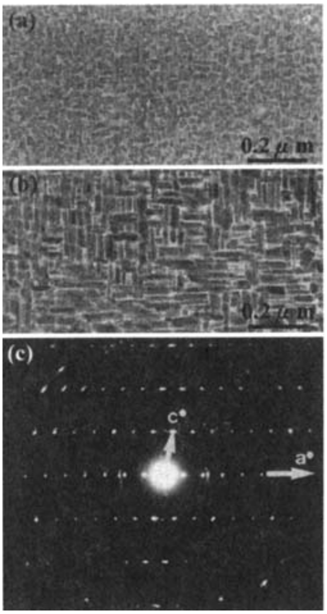

FIGURE 4 Typical TEM images of QD films deposited at 20℃ (a) and 100℃(b), and the electron diffraction pattern(c).

the lattice spacing of 1.41nm and 0.61nm crossing at 102° . These parameters of QD crystal in thin film are different from those of QD bulk crystal obtained with x-ray investigation [2, 4-6]. This also indicates that QD molecules take same orientation in vapor-deposited films, which is different with the crystal structure in bulk QD. The high resolution AFM observation of QD film gave out the lattice fringes with 1.60nm and 0.6nm, which is coincided well with the lattice spacing results of TEM. According to the structural analysis of TEM and AFM, it is considered that QD molecules oriented obliquely to the substrate with the molecular plane composed of carbonyl and amido groups, the molecular stacking column axis is parallel to the substrate surface. On the other hand, as reported priviously [1], the QD-Me took two kinds of orientations on the KBr substrate depended on the substrate temperature. QD-Me molecules in plate-like crystal obtained at a high substrate temperature, orientated parallel to the substrate surface with their molecular planes. While in rod-like crystals formed below 150 substrate temperature, the long axes of the QD-Me molecules oriented parallel to the substrate surface, the short axes stood obliquely at about 55° , just like the situation of the QD molecules. The difference of crystal structure in QD and QD-Me is considering to be closely related to the different degree of hydrogen-bonding in QD and QD-Me films, as discussed above.

Acknowledgments

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