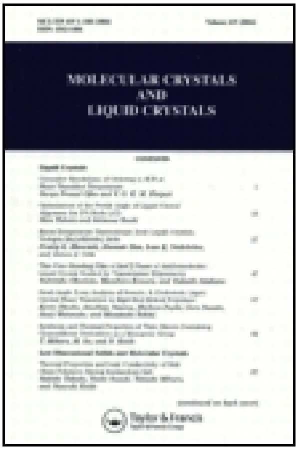

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Epitaxial Relationships of Vapor Deposited Thin Films of Octithiophene on KBr (001)

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The epitaxial relationships of vapor deposited thin films of octithiophene onto KBr (001) were investigated by X-ray diffractometry. The temperature dependence of the film structure was examined between 25°C and 125°C. Two kinds of orientations, standing (100) and lying (51–1), were observed and the former orientation preferentially occurred at higher temperatures. The epitaxial relationships of both standing and lying orientations were determined. The observed epitaxial relationships were explained in terms of misfit ratio.

Keywords: epitaxial relationships; in-plane orientation; octithiophene; X-ray diffraction

INTRODUCTION

Oligothiophenes and their derivatives are currently attracting great attention as potentially useful materials for opto-electronic devices

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such as field-effect transistors and solar cells [1]. Octithiophene (8T) is the longest oligothiophene that can be synthesized and isolated as a pure crystalline compound [2], and it is classified among the organic p-type semiconductors. The studies concerning to carrier transport properties in field-effect transistors and photovoltaic properties using 8T have been reported [3–7]. To optimize such device performances, the orientation control of the molecules in the thin film state is demanded, because their optical and electrical properties reportedly show significant anisotropy depending on the molecular orientations [6]. To control the molecular orientations, the roles of substrates and growth conditions in physical vapor deposition process should be investigated. Generally, organic thin films epitaxialy grow onto the alkali halide substrates such as KCl and KBr by a physical vapor deposition process, and molecular orientation are varied depending on substrate temperatures and deposition rates. In this study, the dependence of substrate temperature on the molecular orientations and epitaxial relationships of vapor deposited thin films of 8T onto KBr (001) was investigated by X-ray diffractometry.

EXPERIMENTAL

The synthesis and purification of Octithiophene (8T) are performed according to a method described elsewhere [8]. Its purification is carried out by slow vacuum sublimation to obtain crystalline bright-red powder (mp = 370°C). Thin films of 8T were fabricated by vacuum deposition in a pressure of 5×10^{-5} Pa using K-cell type crucible kept at 230°C. The substrates used were air-cleaved (001) planes of KBr maintained at a temperatures 25 or 125°C after baked at 200°C for 1 hour. The deposition rate and final film thickness were 0.1 nm/s and 100 nm, respectively. The As-deposited thin films were characterized using X-ray diffraction in air using an X-ray diffractometer (Regaku Co., ATX-G) which was specially designed for characterization of thin films. A parabolic multiplayer positioned next to the laboratory X-ray source produces high intensity parallel beam (Cu Kα). The goniometer has not only usual $\omega/2\theta$ axes but also in-plane $\phi/2\theta\chi$ axes for measuring both in-plane and out of plane diffraction. The details of the diffractometer and characterization method were described elsewhere [9].

RESULTS AND DISCUSSION

Figure 1 shows the conventional $\theta/2\theta$ scan pattern of deposited 8T films on KBr (001) substrates at 25 and 125°C. The lattice parameters

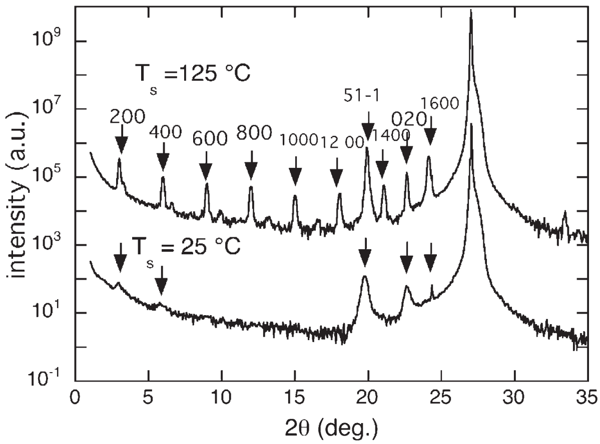

FIGURE 1 Temperature dependence of $\theta/2\theta$ XRD patterns of deposited thin films of 8T on KBr (001) substrate.

of a bulk single crystal of 8T is monoclinic, space group is $P2_1/a$, $a = 5.892\,\mathrm{nm}$, $b = 0.784\,\mathrm{nm}$, $c = 0.600\,\mathrm{nm}$ and $\beta = 90.3^\circ$ [10]. On comparison of the observed lattice spacings and the calculated ones, the diffraction peaks in Figure 1 could be indexed as shown in the figure. The standing (100) orientations and lying (51–1) and (010) orientations appeared depending on temperature. The lying (51–1) and (010) orientations preferentially appeared at a temperature of 25°C. With increasing temperature to 125°C, the standing orientation, (100) planes parallel to the surface, increased as seen $h00$ peaks in the Figure 1. Figure 2 shows the cross sectional view of the (100) and (51–1) orientations.

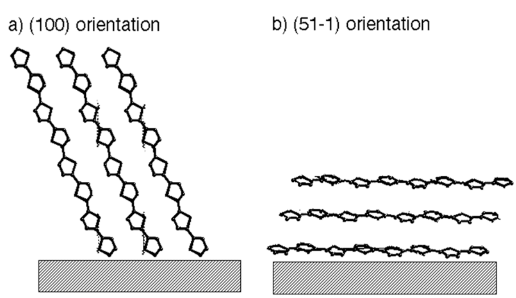

FIGURE 2 Schematic illustration of cross sections of standing (100) and lying (51–1) orientations.

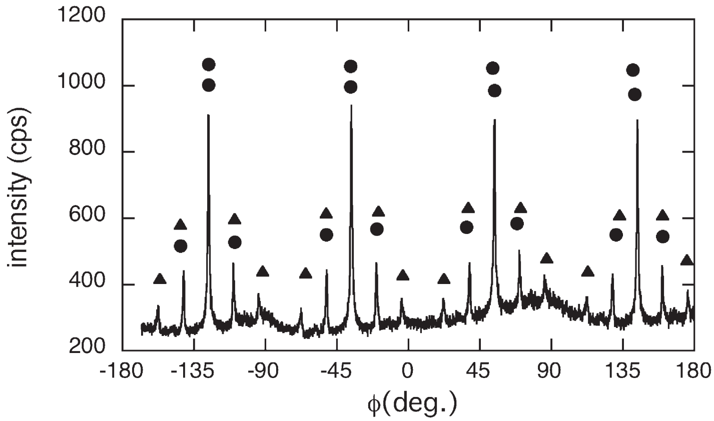

FIGURE 3 In-plane ϕ scan pattern of 51–1 X-ray diffractions of standing (100) orientation ingredients of 8T thin films. Found two kinds of in-plane orientations were denoted by different marks.

As to the in-plane structure, clear epitaxial relationships were found in both standing and lying orientations. Figure 3 shows a pattern of 51 – 1 diffractions from the standing (100) orientation ingredients of 8T films formed at 125°C. In this figure, the intensities of 51 – 1 reflections were plotted as a function of the azimuth rotation angle ϕ. From the patterns, the epitaxial relationships were determined as shown in Figure 4. The determined relationships was $[011]_{8T}//\langle 110\rangle_{KBr}$ and $[011]_{8T}//\langle 100\rangle_{KBr}$. As shown in Figure 4, there exist one-dimensional lattice coordination (lattice matching of point-on-line type) in [110] or [100] directions of KBr, and the misfit ratios between periodicities of 8T and substrate lattices are −4.0% and 1.3% respectively.

The epitaxial in-plane orientation was also found in the lying orientation ingredients. Figure 5 shows the 16 0 0 diffraction pattern from the lying (51–1) orientation ingredients. As shown in this figure, an obvious epitaxial in-plane orientation was seen in the (51–1) orientation ingredients. The corresponding epitaxial relationships were depicted in Figure 6. As shown in this figure, the molecular axis direction [105] nearly parallels the ⟨110⟩ of KBr. As to another lying orientation of (010), no 16 0 0 peak was observed in azimuth ϕ scans. This suggests that the (010) orientation ingredients are not oriented in the plane.

Comparing the epitaxial behavior of 8T with that of para-sexiphenyl (6P) [11], a common rule concerning the epitaxy of deposited organic

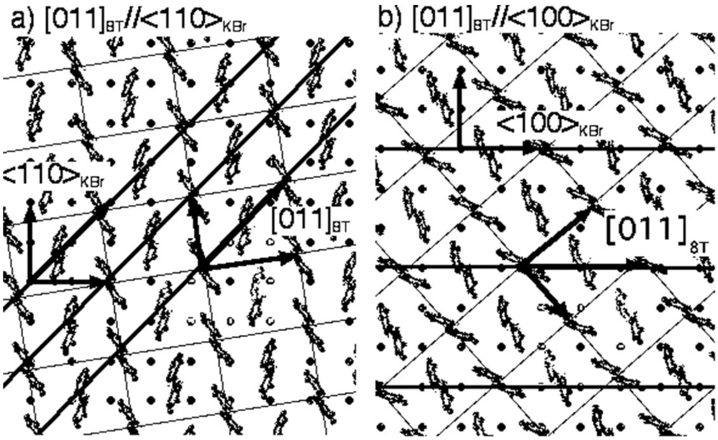

FIGURE 4 Schematic representations of epitaxial relationship between 8T (100) orientation and KBr (001). a: $[011]_{8T}//\langle 110\rangle_{KBr}$, b: $[011]_{8T}//\langle 100\rangle_{KBr}$

films on the alkali halide substrates emerged. In the case of 6P, three kind of in-plane orientations for the standing orientation ingredients and two kind of in-plane orientations for the lying orientation ingredients have been found depending on the kinds of substrates. All of these have one-dimensional lattice matching and the misfit ratios were less than 4%. In the case of 8T, the misfit ratios of observed in-plane orientations were also less than 4%. The small amount of

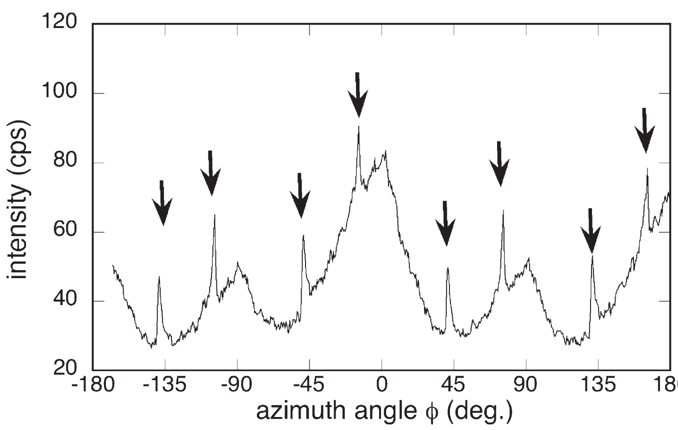

FIGURE 5 In-plane ϕ scan pattern of 1600 X-ray diffractions of lying (51$-$1) orientation ingredients of 8T thin films.

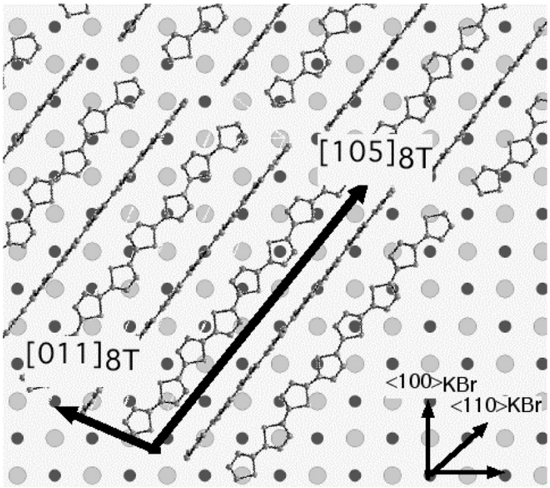

FIGURE 6 Schematic representation of epitaxial relationship between 8T (51 −1) orientation and KBr (001).

misfit ratio should because of preferential nucleation of the clusters having a particular direction against the direction of substrate single crystals.

The orientation control technique shown in the present study will be useful for improvement in the properties of organic electronic devices such as field-effect transistors and solar cells. In the transistors, the standing orientation would be desirable because the overlap of π-orbital in lamella plane brings higher carrier mobility. By contrast, laying orientations are desirable in solar cells because horizontally oriented 8T molecules harvest light more efficiently. Furthermore, application of epitaxy in organic electronic devices would greatly improve the performance of such devices.

CONCLUSIONS

The crystal orientations of vacuum deposited thin films of octithiophene (8T) onto KBr (001) were determined by using X-ray diffraction. The lying (51 −1) and (010) orientations preferentially occurred at lower substrate temperatures, and the standing (100) orientation appeared with increasing temperature. The epitaxial relationships of (51 −1) and (100) orientations were successfully determined. Small amount of misfit ratio seems to lead such particular in-plane orientations.

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