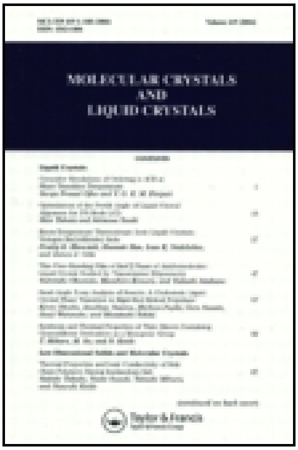

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Epitaxial Relationships of Pentacene Polymorphs on KCl (001)

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Epitaxial relationships of pentacene polymorphs on KCl (001) were investigated by X-ray diffractometry and adsorption energy calculation. The in-plane and out-of-plane structures of the deposited thin films were investigated using a four-axes X-ray diffractmeter. Two polymorphs, bulk and thin film phases, appeared and the in-plane orientations were determined for each polymorph. The adsorption energies of clusters including four pentacene molecules were successfully calculated as a function of rotation angle and the results were well consistent with the experimental data.

Keywords: epitaxial relationships; pentacene; polymorph; potential energy calculation

INTRODUCTION

Organic thin film transistors (OTFTs) have made extremely rapid progress in the last several years. However, many problems still remain as the barriers to use OTFTs in ubiquitous electronic devices. To improve the performance of such devices, orientation control of the molecules in the thin film state is very important, because the physical

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properties of organic semiconductors show significant anisotropy and depend on the density of grain boundaries. It is well known that organic thin films epitaxialy grow onto the alkali halide substrates such as KCl by a physical vapor deposition process. Taking advantage of the epitaxial growth, the orientation control of molecules should be achieved, and we have so far studied the epitaxial relationships between deposited organic thin films and alkali halide substrates by X-ray diffractometry [1–3].

Pentacene is a representative organic semiconductor as the promising material for use in OTFT [4]. It has mainly two polymorphic modifications, thin film phase and bulk phase, in its vapor deposited thin films. The both crystal structures were categorized in triclinic system, and the lattice constants were reported as $a = 7.93\,\text{Å}$, $b = 6.14\,\text{Å}$, $c = 16.03\,\text{Å}$, $\alpha = 101.9^\circ$, $\beta = 112.6^\circ$ and $\gamma = 85.8^\circ$ for the bulk phase, and as $a = 6.1\,\text{Å}$, $b = 7.6\,\text{Å}$, $c = 15.3\,\text{Å}$, $\alpha = 81.0^\circ$, $\beta = 85.0^\circ$ and $\gamma = 95.5^\circ$ for the thin film phase [5,6]. In this study, to clarify the mechanism of epitaxy, the epitaxial relationships of pentacene polymorphs on KCl (001) were investigated by X-ray diffractmetry and calculation of adsorption energy. The adsorption energy of a cluster including four molecules was successfully calculated as a function the directions of in-plane orientation and the experimentally observed expitaxial relationships were fully explained by a model used in the calculation.

EXPERIMENTAL AND CALCULATION METHOD

Thin films of pentacene were fabricated by vacuum deposition in a pressure of 5×10^{-5} Pa using K-cell type crucible. The substrates used were air-cleaved (001) planes of KCl maintained at a 50°C. The deposition rate and final 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 paralleal beam (Cu Kα). The goniometer has four axes for measuring both in-plane and out-of-plane diffraction. The details of the diffractometer and characterization method were described elsewhere [1].

The adsorption energy of the cluster that consisted of four pentacene molecules on the KCl (001) surface was calculated using the 6-12 Lennard-Jones potential. The employed equation of 6-12 Lennard-Jones potential is follows;

$$U_{ij} = \left(\frac{B_{ij}}{r_{ij}^{12}}\right) - \left(\frac{A_{ij}}{r_{ij}^{6}}\right). \tag{1}$$

Where, r_{ij} is the distance between atom i in pentacene molecules and ion j in KCl. The attractive energy constant A_{ij} was determined by using the following equation;

$$A_{ij} = \sqrt{A_{ii}A_{jj}}. \tag{2}$$

Here, the attractive energy constants between same atoms A_{ii} and A_{jj} were introduced from the references [7–9]. The repulsive energy constants B_{ij} is calculated from condition that U_{ij} is a minimum at the equilibrium distance, which is the sum of the ionic radii for ions in KCl and the van der Waals radii for C and H in the pentacene molecule [7,10]. Total potential energy were calculated by summing over all atoms in the pentacene and ions in the KCl substrate using the Eq. (1). The atomic coordinates of the pentacene molecules were chosen from X-ray structure data [5]. The cluster was consisted of four pentacene molecules having the same configurations as crystal structures as shown in Figure 1. The potential energy of cluster was calculated as a function of rotating angle ϕ on the xy-plane of KCl. The ϕ is defined as zero when the geometry of $[100]_{\mathrm{pentacene}}//\!<110>_{\mathrm{KCl}}$. The cluster height z was determined where the one of the nearest molecule in the cluster contacts to KCl substrate.

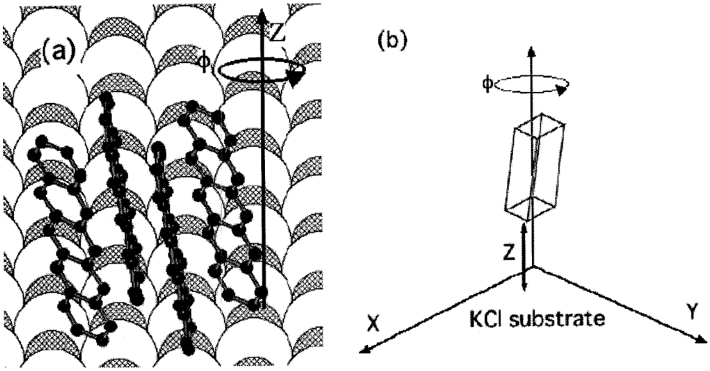


FIGURE 1 A model for adsorption energy calculation of pentacene cluster on KCl substrate. The rotation angle ϕ is defined as zero when the geometry of [100]pentacene//<110>$_{\mathrm{KCl}}$.

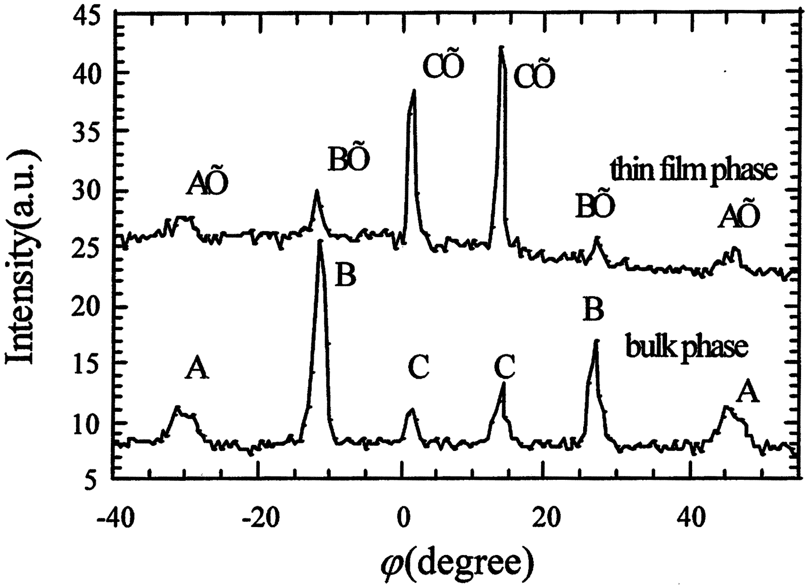


FIGURE 2 In-plane X-ray diffraction pattern of pentacene polymorphs as a function of azimuth angles φ.

RESULTS AND DISCUSSION

Figure 2 shows the in-plane (111) X-ray diffraction data form the two polymorphs of pentacene thin films on KCl (001). From these XRD data, the epitaxial relationships were successfully determined as summarized in the Table 1. Both bulk phase and thin film phase showed the three kinds of epitaxial relationships. For convenience, we named these relationships as A, B, and C, and A′, B′ and C′ for the bulk and thin film phases, respectively.

Figure 3 shows angular dependence of the calculated potential energies of clusters of pentacene polymorphs on KCl surface. As to the bulk phase, three minimums appeared at $\phi = 13^\circ$, 29° and 45° as shown in

TABLE 1 Determined Eptaxial Relationships of Pentacene on KCl

Polymorphs	Eptaxial relationships
Bulk	A: $(001)_{\mathrm{pen}}$.//$(001)_{\mathrm{KCl}}$, $[210]_{\mathrm{pen}}$.//<100>$_{\mathrm{KCl}}$ B: $(001)_{\mathrm{pen}}$.//$(001)_{\mathrm{KCl}}$, $[-130]_{\mathrm{pen}}$.//<110>$_{\mathrm{KCl}}$ C: $(001)_{\mathrm{pen}}$.//$(001)_{\mathrm{KCl}}$, $[010]_{\mathrm{pen}}$.//<100>$_{\mathrm{KCl}}$
Thin film	A′: $(001)_{\mathrm{pen}}$.//$(001)_{\mathrm{KCl}}$, $[110]_{\mathrm{pen}}$.//<130>$_{\mathrm{KCl}}$ B′: $(001)_{\mathrm{pen}}$.//$(001)_{\mathrm{KCl}}$, $[120]_{\mathrm{pen}}$.//<110>$_{\mathrm{KCl}}$ C′: $(001)_{\mathrm{pen}}$.//$(001)_{\mathrm{KCl}}$, $[010]_{\mathrm{pen}}$.//<100>$_{\mathrm{KCl}}$

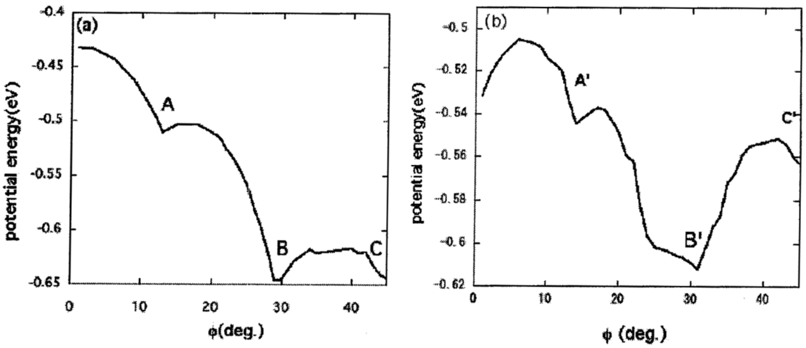
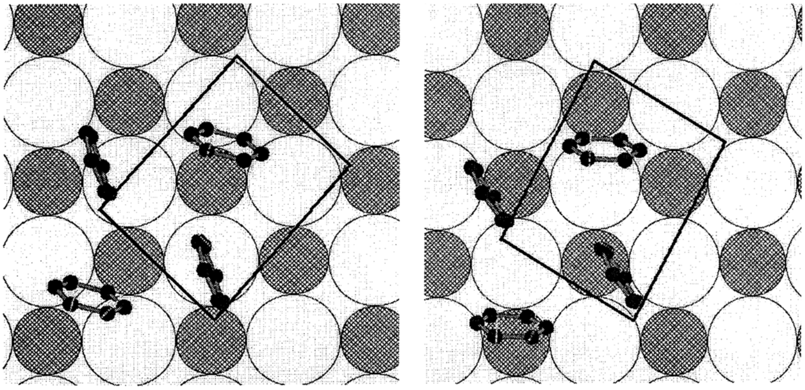
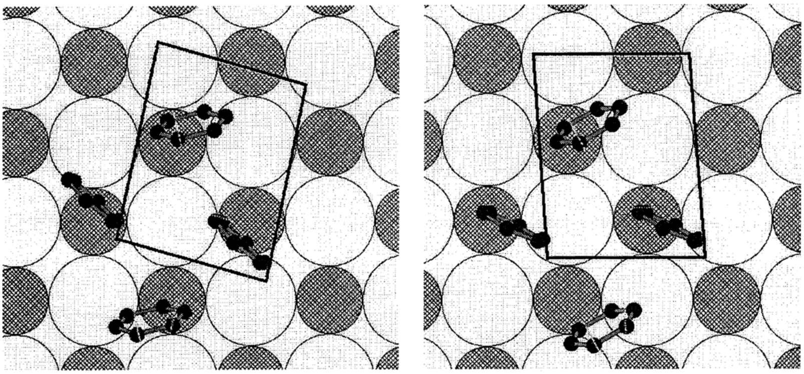


FIGURE 3 Angular dependence of potential energy of pentacene clusters on KCl substrates. (a); bulk phase (b); thin film phase.



(a) Start point (φ=0°)

(b) A (φ=13°)



(c) B (φ=29°)

(d) C (φ=45°)

FIGURE 4 Schematic illustrations of epitaxial relationships of bulk phase of petancene and KCl substrate.

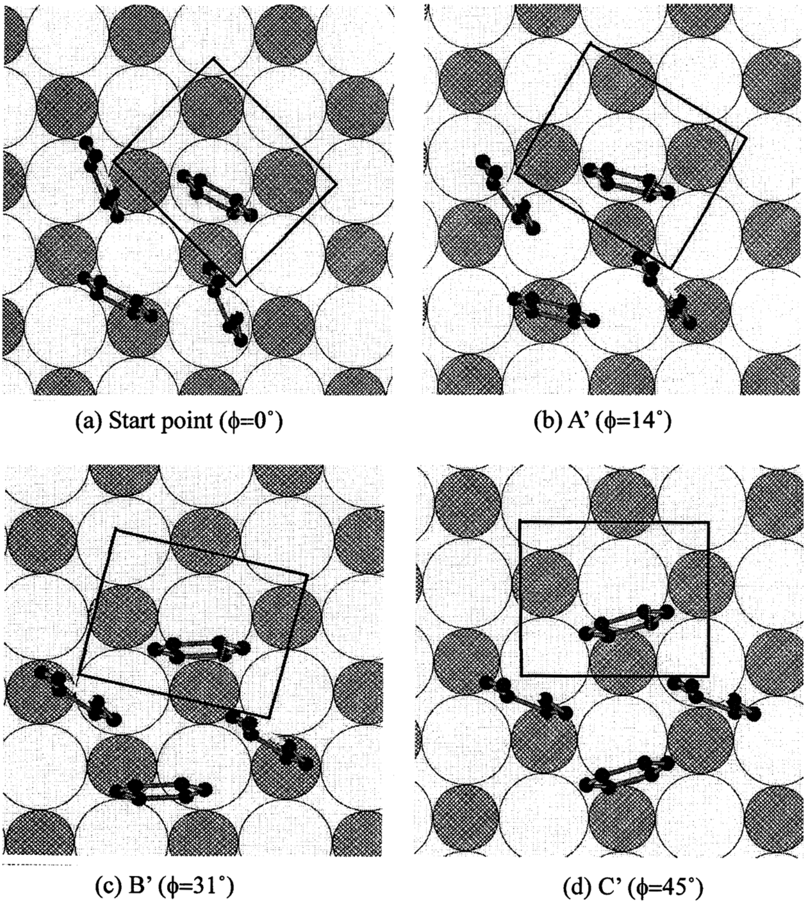


FIGURE 5 Schematic illustrations of epitaxial relationships of thin film phase of pentacene and KCl substrate.

Figure 3(a). These positions considerably correspond to the experimentally determind A, B and C positions in Table 1, respectively. In the case of thin film phase (Fig. 3(b)), three minimums also appeared at $\phi = 13^\circ$, 32° and 45°. These also correspond to the positions of A′, B′ and C′ in Table 1, respectively. The schematic illustrations of observed epitaxial relationships were depicted for the bulk and thin film phases in Figures 4 and 5. As shown in these figures, in the stable states, each molecule in the clusters takes the position at the space between K^+ and/or Cl^- ions on the surface. This is because the distance between the cluster and substrate becomes minimum at these positions. Hence, the epitaxial relationships observed in pentacene polymorphs on KCl could be explained by a simple model that in-plane orientation dependent adsorption energy of small clusters determine the epitaxial relationship of the deposited thin films through the easiness of nucleation.

CONCLUSIONS

The epitaxial relationships of vapor deposited pentacene thin films onto KCl (001) substrates have been investigated by X-ray diffractmetry and calculation of adsorption energy. The angular dependence of the adsorption energies of pentacene clusters show three minimum positions, which are fully consistent with the experimental results of the epitaxial relationships obtained from in-plane X-ray diffraction data. The observed behavior of epitaxial relationships of pentacene and KCl could be explained by a simple cluster model.

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