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On the coexistence of different polymorphs in organic epitaxy: α and β phase of PTCDA on Ag(1 1 1)

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Abstract

The structure and epitaxy of thin films of PTCDA (3,4,9,10-perylenetetracarboxylic dianhydride, $C_{24}H_8O_6$) grown at 180°C on Ag(1 1 1) have been studied in situ using grazing-incidence X-ray diffraction. An extensive map of Bragg reflections has been recorded. A pronounced peak splitting is found, which provides evidence for the coexistence of α and β-like polymorphs,

Keywords: Surface X-ray diffraction; Surface crystallography; Organic thin films; Epitaxy

1. Introduction

Several of the planar organic compounds form rich and complex structures with well-defined epitaxy when grown as thin films on suitable substrates. Examples include perylene- and pentacene-derivatives, oligothiophenes, and phthalocyanines grown by organic molecular beam epitaxy (OMBE) [1]. In many of these systems electrostatic intermolecular interactions and van der Waals forces are important for determining the structure, as opposed to strong covalent or metallic bonding with the substrate as in inorganic epitaxy. Most studies have been motivated by a broad range of potential applications which include optoelectronic devices, chemical sensors, coatings, etc. Furthermore, these systems hold promise for new applications which exploit their unique elastic and epitaxial properties, such as for the elastic modification of metal or semiconductor heterostructure interlayers and for synthesis of lattice-mismatched epitaxial systems via coupling across a van der Waals bonded layer, a process which has been recently termed ''xenotaxy'' [2].

One of the problems frequently encountered is the rich polymorphism, as it is found in a model system for OMBE, PTCDA (3,4,9,10-perylenetetracarboxylic dianhydride, $C_{24}H_8O_6$). These possible structural complications as well as their strong impact on the optical and electronic properties [1,3] make a thorough characterization of the growth and epitaxy of these systems mandatory.

In order to understand the growth mode, crystallography, and temperature behavior (including the separate roles of strain and epitaxial clamping) of thin

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films of PTCDA on Ag(1 1 1), an extensive in situ grazing-incidence X-ray diffraction (GIXD) study [4] has been performed. This paper focuses on GIXD results from PTCDA grown epitaxially on Ag(1 1 1) in the high temperature growth regime. The results from other methods and for other preparation conditions including the temperature-dependent transition to island growth will be published in a forthcoming paper [5].

2. Bulk and film structures of PTCDA

In bulk form PTCDA crystallizes as stacked molecular sheets, each plane containing interlocking PTCDA molecules in a herringbone structure. Two monoclinic polymorphs have been observed, denoted as the α phase ($a = 3.74$ Å, $b = 11.96$ Å, $c = 17.34$ Å, $\beta = 98.8°$) [6,7] and the β phase ($a = 3.87$ Å, $b = 19.30$ Å, $c = 10.77$ Å, $\beta = 83.6°$) [8,9]. The notation used here refers to the bulk α phase. For thin films the preferred growth planes are the (1 0 2) lattice planes shown schematically in Fig. 1. Assuming bulk-like lattice parameters, the arrangement of the molecules in the (1 0 2) lattice planes can be described by a rectangular 2D unit mesh with the dimensions $b_1^\alpha = 11.96$ Å and $b_2^\alpha = 19.91$ Å for the α phase, and $b_1^\beta = 12.45$ Å and $b_2^\beta = 19.30$ Å for the β phase.

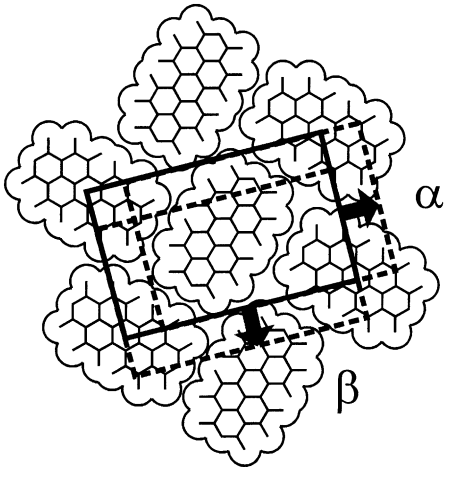

Fig. 1. Schematic diagram of PTCDA on Ag(1 1 1), which shows the interlocking herringbone structure within PTCDA (1 0 2) planes parallel to the surface. Also indicated are the positions of the second layer (projected in the 2D plane; broken lines), which stacks such that in the α phase the quadrangle is translated laterally along the long axis of the in-plane unit cell whereas in the β phase it is translated along the short axis.

While these quantitative differences of the 2D unit cell in the (1 0 2) plane are small, a qualitative difference is found in the stacking direction. For the α phase, the 2D unit cell in the second molecular sheet is translated along the long axis of the molecular sheet underneath, whereas for the β phase it is translated along the short axis (Fig. 1). In a diffraction experiment, this implies that for Bragg reflections at a given in-plane momentum transfer, $q_\parallel$, the dependence on the out-of-plane momentum transfer, q_z, has to be investigated. Neither measurements purely in the 2D plane nor purely along the surface normal (i.e. the (1 0 2) Bragg peak) are sufficient to detect the qualitative difference of α and β phase. In view of this rather complicated structure, which depends strongly on the substrate and the preparation conditions, it is not surprising that, despite numerous studies [1,8–12], no clear picture of the epitaxial phase behavior has evolved in the literature.

3. Experimental

The experiments were carried out at beamline ID10B of the European Synchrotron Radiation Facility (ESRF) at a wavelength of 0.9 Å. Extensive GIXD scans have been performed using a six-circle diffractometer in horizontal z-axis geometry in combination with a position sensitive detector oriented along the q_z-direction. The analysis of the data was based on 31 separate GIXD peaks, as well as measurements of the (1 0 2) peak oriented along the specular direction.

The film preparation and the in situ GIXD experiments were performed in a portable, diffractometer-based OMBE chamber, which is described in detail elsewhere [13]. We review it only briefly here. It is a full-featured system for organic molecular beam epitaxy, but small enough to be mounted directly on a diffractometer table. It includes a sample heater, sputter gun, evaporation sources, quartz crystal thickness monitor, and capabilities for sample cooling. A 360° beryllium window permits in situ, real-time X-ray diffraction measurements to be carried out during growth. Pressures in the 10^{-10} mbar range are achievable via a top-mounted turbomolecular

pump and a side-mounted battery-powered ion pump, which can maintain vacuum during transport to a synchrotron beamline.

The Ag(1 1 1) substrate was carefully cleaned before growth by repeated cycles of Ar^+ sputtering and annealing. In what follows we present measurements of thin films of 200 Å of PTCDA, prepared at temperatures of about 180°C and growth rates of 3.5 Å/min. The GIXD measurements were taken at room temperature.

4. Results and discussion

PTCDA grows on Ag(1 1 1) with its (1 0 2) stacking direction along the surface normal, as previously reported for other systems. A simplified picture of the reciprocal lattice is shown in Fig. 2. We define the azimuthal orientation of the 2D unit cell by the in-plane projection of the (0 1 2) peak at $\phi = 0$, which is along the azimuthal direction of the Ag(2 2 $\overline{4}$) bulk reflection. The PTCDA (0 1 $\overline{2}$) peak is expected at an azimuthal orientation [10]

$$\delta\phi = \phi_{0\,1\,\overline{2}} - \phi_{0\,1\,2} = 2\arctan\left(\frac{2b_1}{b_2}\right) \quad (1)$$

away from the (0 1 2) peak. Due to the substrate symmetry giving rise to six equivalent domains labelled by superscripts (a, b, c, d, e, and f), we expect a symmetry-equivalent (0 1 $\overline{2}$) reflection ($n \times 60° - \delta\phi$) away from the (0 1 2) peak. Using the above bulk parameters for b_1 and b_2 we thus expect an azimuthal position of the $(0\,1\,\overline{2})^{c}$ and the $(0\,1\,\overline{2})^{d}$ peak relative to the $(0\,1\,2)^{a,b}$ peak at $\phi^{\alpha} = \pm 19.45°$ (with $q_z = 0.3733\,\text{Å}^{-1}$) for the α phase and at $\phi^{\beta} = \pm 15.76°$ (with $q_z = 0.3344\,\text{Å}^{-1}$) for the β phase.[2]

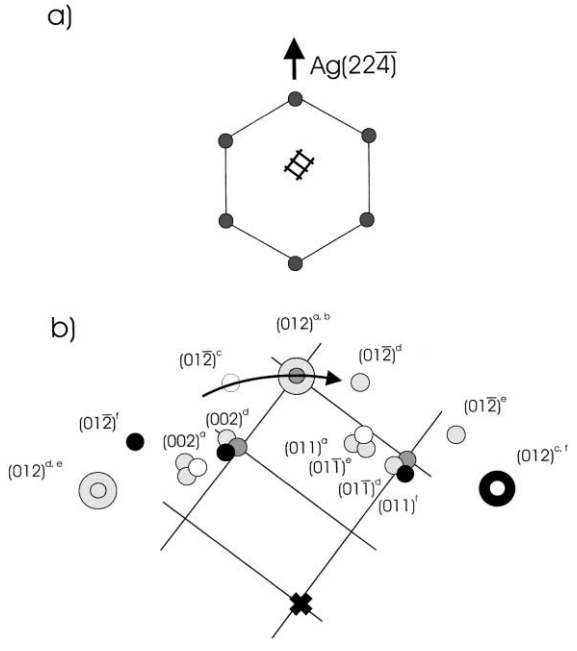

Fig. 2. Simplified reciprocal space of PTCDA(1 0 2)/Ag(1 1 1) in α phase notation. The six PTCDA domains shown are labeled a, b, c, d, e, and f. Part (a) shows how the PTCDA peaks (shown in more detail in part (b)) are situated in relation to the Ag unit mesh (the filled cycles are the Ag surface peaks). PTCDA(0 1 2) is aligned parallel to Ag(2 2 $\overline{4}$). The curved arrow in (a) indicates the direction of the azimuthal scan in Fig. 3.

Fig. 3(a) shows wide angle azimuthal scans for two different values of q_z through the (0 1 2) peak as shown schematically by the curved arrow in Fig. 2. While Fig. 2 suggests only two reflections in this area, the scan actually reveals a more complex pattern. For simplicity, we will base our peak assignment on the bulk phases (α and β), although from the absolute peak locations we know that the structures found in our films are strained with respect to these [5]. As we will explain below, the pattern in Fig. 3 provides evidence for two inequivalent orientations of the α phase and another two inequivalent orientations of the β phase.

Substrate imperfections can be ruled out as a reason for this peak splitting, since the Bragg reflections from the single-crystal substrate are not split and only $\leq 0.1°$ in width. Moreover, the conclusions reported below are consistent with all other PTCDA reflections (like (0 1 1), (0 0 2), etc.) including their respective splittings, which will be analyzed in more detail elsewhere [5]. In the present short paper, we will focus on the (0 1 2) and the (0 1 $\overline{2}$) peaks. We note that possible small differences in the in-plane momentum transfer, $q_{\|}$, of the (0 1 2) and the (0 1 $\overline{2}$) peak (which can arise from a non-rectangular in-plane unit cell) are neglected for simplicity.

We rationalize the azimuthal positions of the various reflections as follows. Based on the azimuthal spacings calculated from the bulk parameters

[2] The (0 1 2) Bragg reflection in α phase notation corresponds to the (0 2 1) Bragg reflection in β phase notation.

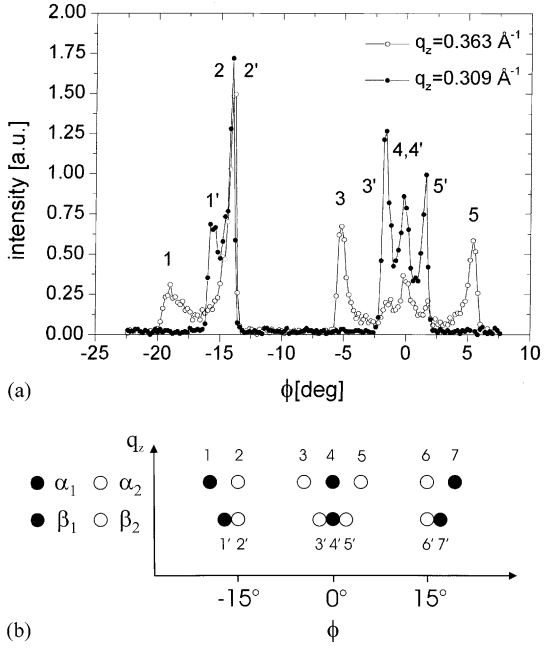

Fig. 3. (a) Azimuthal in-plane scan through the PTCDA(0 1 2) reflections as indicated by the arrow in Fig. 2. Two scans for different q_z values are shown. The azimuthal angle $\phi = 0$ corresponds to the Ag(2 2 $\overline{4}$) direction. (b) Schematic representation of the measured (0 1 2) and (0 1 $\overline{2}$) reflections as a function of ϕ and q_z. See text for the peak assignment.

($\phi^{\alpha} = \pm 19.45°$ and $\phi^{\beta} = \pm 15.76°$), the peaks 1 and 1′ are assigned as (0 1 $\overline{2}$) peaks of the α and the β phase, respectively, with their corresponding (0 1 2) reflections being located at $\phi = 0$ (two overlapping peaks labelled 4,4′) (see footnote). This assignment is further supported by their dependence on q_z, showing that the signal of peak 1 vanishes for the smaller q_z, consistent with what is expected from the bulk. Thus, the data provide evidence for a coexistence of the two bulk polymorphs in the epitaxial thin film.

For the assignment of the other reflections in Fig. 3(a), it is helpful to refer to Fig. 3(b), which schematically displays all measured peaks around the (0 1 2) reflection as a function of azimuthal orientation and q_z. Four reflections are found in the azimuthal region of the (0 1 $\overline{2}$)[c] peak (around $\phi = -15°$) and six in the region of the (0 1 2)[a,b] peak (around $\phi = 0$). In order to illustrate the symmetry, Fig. 3(b) also includes the region of the (0 1 $\overline{2}$)[d] peak (around $\phi = +15°$).

The reflections can be separated into two groups according to their q_z values. Using the nomenclature as introduced in Fig. 3, the peaks (1, 2,. . .,7) found around $q_z = 0.363\,\text{Å}^{-1}$ belong to the first group, the other peaks around $q_z = 0.309\,\text{Å}^{-1}$ to the second group. By analyzing the peak shape and intensity we can sort the peaks further. The first group separates in (1,4,7) and (2,3,5,6), the second in (1′,4′,7′) and (2′,3′,5′,6′). From the mirrorlike distortion of the peaks, for example of peak (3,5) and (3′,5′), and their symmetric arrangement around $\phi = 0$, we conclude that these reflections belong to mirror domains while every pair [(2,5), (1,4), (2′,5′), and (1′,4′)] belongs to one domain. We obtain an azimuthal spacing of 19° for (2,5) and (1,4), whereas we measure 15.6° for (2′,5′) and (1′,4′). These values deviate only slightly from the values expected for the bulk α and β phase, respectively. Furthermore, the peaks separated by 19° have a larger q_z than the other peaks as expected for the α phase compared to the β phase.

In conclusion, the peak splitting provides evidence for two inequivalent α and two inequivalent β phase domains (α_1, β_1, α_2, and β_2). α_1 and β_1 denote those phases, which appear with their (0 1 2) reflection at $\phi = 0$ along the Ag(2 2 $\overline{4}$) direction, whereas α_2 and β_2 denote those which appear away from this high-symmetry direction:

α_1 PTCDA(0 1 2) at $\phi = 0$ ($\parallel$ Ag(2 2 $\overline{4}$))

β_1 PTCDA(0 1 2) at $\phi = 0$ ($\parallel$ Ag(2 2 $\overline{4}$))

α_2 PTCDA(0 1 2) at $\phi = \pm 5°$

β_2 PTCDA(0 1 2) at $\phi = \pm 1.5°$

Since the oblique angles of α_2 and β_2 are mutually related (via the common azimuthal orientation of peak 2 and 2′), one might speculate that one phase grows on top of the other. α_1 and β_1 might be related in a similar fashion. The role of the preparation conditions as well as the substrate miscut will be subject of future studies [5].

5. Summary

The crystal structure and epitaxial orientation of 200 Å thick films of PTCDA grown at elevated temperatures (180°C) on Ag(1 1 1) substrates has been

investigated by in situ grazing-incidence X-ray diffraction, using a portable, diffractometer-based OMBE deposition system. A large number of Bragg reflections has been measured. Based on the multiple-peak features around the PTCDA (0 1 2) reflection, we have provided evidence that the structure actually consists of versions of the bulk α and β polymorphs, slightly modified by epitaxial strain. It is noted that α_1 and β_1 domains as well as α_2 and β_2 domains are aligned with one axis, leading to the speculation that one domain possibly overgrows the other. The results underline that the epitaxy of these compounds, while being well-defined, can be highly non-trivial and that care has to be taken when, e.g. optical spectra are correlated with structural data. Growth studies performed at different rates and temperatures, as well as studies which address the temperature-dependent behavior and real-space morphology are in progress and will be presented elsewhere [5].

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