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# Analysis of the three-dimensional structure of a small crystallite by scanning tunneling microscopy: Multilayer films of 3, 4, 9, 10-perylenetetracarboxylic-dianhydride (PTCDA) on Cu(110)

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PACS. 68.55.Jk – Structure and morphology; thickness; crystalline orientation and texture.

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PACS. 81.15.Hi – Molecular, atomic, ion, and chemical beam epitaxy.

**Abstract.** – The growth of 3,4,9,10-perylenetetracarboxylic-dianhydride (PTCDA) on Cu(110) has been investigated by STM in the range of a few up to more than 20 molecular layers. It is found to grow in the Stranski-Krastanov mode leading to well-ordered mesa-type crystalline grains of different structure and orientation relative to the substrate. By operating a scanning tunneling microscope at a low tunneling current of 2 pA, we were able to resolve the individual molecules on the flat top of the crystallites as well as on the facets descending to the substrate. As will be shown, this offers the unique possibility to determine unambiguously the three-dimensional structure. For a given grain a detailed analysis will be presented yielding the unit cell and the relative displacement between subsequent layers.

*Introduction.* – Scanning tunneling microscopy offers the unique possibility to analyze in real space the arrangement of atoms or molecules at a surface. This has been first demonstrated by Binnig *et al.*, *e.g.*, for the Si(111)  $7 \times 7$  surface [1]. Since then this technique has been applied with great success for a huge number of different surfaces. Due to the principle of operation only the outermost layers of the sample may be analyzed. In spite of this limitation the three-dimensional structure of a crystallite may be identified if the facets may be imaged with atomic or molecular resolution. This has been demonstrated for inorganic clusters, *e.g.*, of Ge on Si(100) [2], of Pd [3,4] or Ag [5]. In this paper we present the study of crystallites of organic molecules. The three-dimensional structure which was not known beforehand could be determined from the data obtained by STM. The growth of organic molecules on inorganic substrates is of major interest because of possible application in molecular electronic devices, *e.g.*, organic light-emitting diodes. In order to reduce the recombination of charge carriers it is desirable to obtain a defect-free epitaxial growth on inorganic substrates. Since PTDCA is a rigid, planar and very stable molecule it serves as a prototype for this kind of investigations. Thin layers of PTCDA have been analyzed mainly by low-energy electron diffraction and by scanning tunneling microscopy (STM) for a variety of substrates [6–12].

So far the analysis of organic films by STM has been concentrated on low coverage, *i.e.* monolayers. Only a few examples have been reported for more than one layer. Cuberes *et*

*al.* [13] analyzed  $C_{60}$  on a monolayer of dimethyl-bianthron on Cu(111). Epitaxial growth of two planar molecules has been demonstrated by Schmitz-Hübsch *et al.* [14] for PTCDA on hexabenzocoronene and by Staub *et al.* [15] for PTCDA on decanethiol. A coverage of up to 3.5 monolayers has been analyzed by Chizhov *et al.* [16] for PTCDA on Au(111).

Exploiting the capability of our STM to work at very low tunneling current we report in the present paper on the investigation of PTCDA on Cu(110) at much higher coverage. The films exhibit a very clear example of “Stranski-Krastanov growth”; hence after the formation of one or two monolayers the formation of 3D islands begins. This provides a unique possibility to analyze in detail the structure of multilayers. Since the edges of the islands are sloped, not only the number of layers may be counted but also the relative positions of the different layers may be determined.

*Experimental.* – The experiments have been performed in an ultra-high vacuum system consisting of separate chambers for sample preparation and characterization. The Cu(110) substrate has been prepared by repeated cycles of sputtering of a single crystal with  $Ar^+$  ions (1.4 keV,  $10 \mu A/cm^2$ ) and thermal annealing to 820 K. The result of this procedure was checked by XPS and by STM. The PTCDA molecules have been evaporated from a small self-built crucible kept at a temperature of 510 K providing a flux of about 4 monolayers/min at the sample. Prior to the measurements, the flux of particles has been carefully checked by a quadrupole mass spectrometer. For the results presented in this paper the equivalent of 10–40 monolayers has been deposited. The films have been thermally annealed using a linear temperature ramp (1 K/s) ending at 510 K. This results in a loss of about 10% of the material. The samples have been transferred *in situ* to a home-built STM, which is optimized to provide a minimal electric noise by capacitive pick-up of line frequency etc. In combination with a self-built current-to-voltage converter it allows to operate the STM at a tunneling current down to 1 pA using a bandwidth of 30 kHz. For the given experiments a typical current of 2 pA has been used. The STM was calibrated by the investigation of the clean Cu(110) prior to the measurement of the molecular layers.

*Results.* – If about 20 monolayers of PTCDA are deposited on Cu(110) and if the film is annealed to 510 K, small crystals with a typical size of about 100 nm are formed. They appear as truncated pyramids, which are mostly separated by areas covered by a thin layer of PTCDA, which exhibits no significant order. The top layer always has the form of an irregular hexagon. The orientation and the form vary between the different grains. The slopes are relatively shallow enabling the detailed investigation by STM. Figure 1 displays a crystallite formed by nineteen plus about two wetting molecular layers. Since the conductivity on top is rather low, only a very tiny tunneling current of 1.8 pA at  $U = -2$  V at the tip could be applied. The displayed area is  $94 \times 94 \text{ nm}^2$ ; the height of the formation is about 7.5 nm. The latter cannot be exactly evaluated because the clean substrate cannot be accessed. To analyze the geometric structure, a top view of the same data is given in fig. 2. It can be readily seen that the borderlines of the top layer are parallel to the ones on the opposite site. Furthermore the four angles, which are denoted  $\delta$  in the figure, amount to  $123^\circ$  and agree within the experimental uncertainty.

In order to explain this geometry small areas of the top layer have been investigated in more detail. Figure 3 shows the real-space image (a), the Fourier transform (b) and a tentative model of the molecular arrangement within the unit cell (c). The real-space image as well as the Fourier transform clearly reveal a rectangular unit cell with a dimension of  $a = 12.5 \text{ \AA}$  and  $b = 19.5 \text{ \AA}$ . The short  $a$ -axis is parallel to the rows, which are visible in (a). In the following discussion  $\vec{a}$  will serve as reference to which all other directions will refer. A preliminary analysis shows that the molecular unit cell is rotated by about  $5^\circ$  counterclockwise with

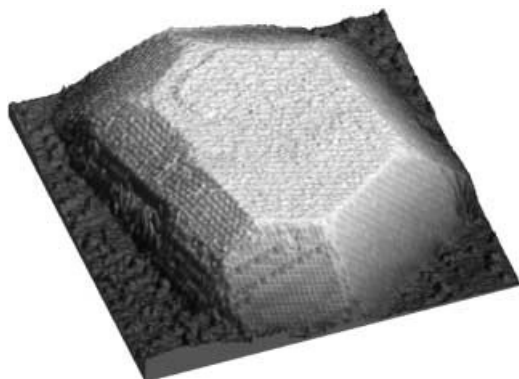


Fig. 1

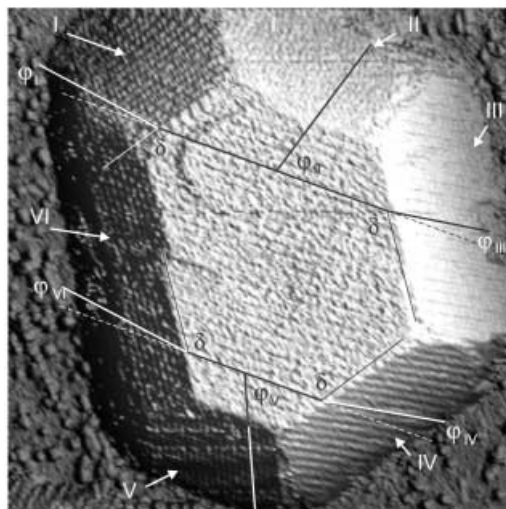


Fig. 2

Fig. 1 – Pseudo–three-dimensional representation of a crystallite of PTCDA grown on Cu(110). The size of the displayed area is  $94 \times 94 \text{ nm}^2$ ; the height of the crystal is approximately 7.5 nm. In order to visualize details of the facets shading has been applied.

Fig. 2 – Top view representation of the data of fig. 1. To analyze the geometric structure, the facets have been labeled; furthermore, various angles have been marked.

respect to the atomic lattice of the substrate, *i.e.*  $\vec{a}$  *vs.*  $[100]$  and  $\vec{b}$  *vs.*  $[1\bar{1}0]$ . Since  $\text{tg } \delta = \frac{b}{a}$ , the geometry of the borderlines is easily understood. Those corresponding to the facets I, III and IV, VI are parallel to the two diagonals; the two other are parallel to the short axis of the unit cell. Boundary lines parallel to the long axis have not been found. The fact that the diagonals act as edge appears plausible if one considers the arrangement of the molecules within the unit cell. Figure 3c shows a model, which agrees with the various observations. There are two molecules per unit cell which are rotated by about  $90^\circ$  with respect to each other. This arrangement is energetically favorable due to the quadrupole moment of the molecule. It resembles the “herringbone structure” found for the  $[102]$ -plane of the bulk structure [17] or, *e.g.*, for monolayers of PTCDA on Ag(111) [10]. However, it should be mentioned that from the observations it was neither possible to evaluate the orientation to a high accuracy nor to exclude a tilt of the molecules with respect to the plane of the unit cell.

The patterns on the different facets indicate that the crystallite is formed by a regular

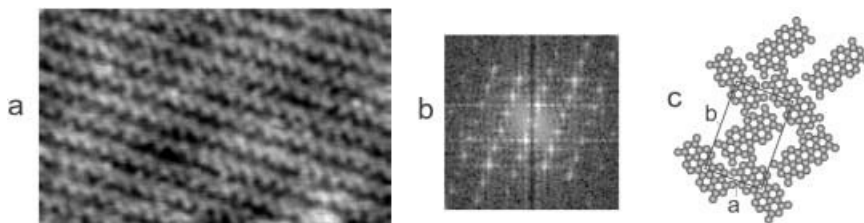


Fig. 3 – Analysis of the top layer: a) topography of an area of  $27 \times 17 \text{ nm}^2$ ; b) Fourier transform displaying the corresponding reciprocal lattice; c) model for the arrangement of the molecules in the top layer.

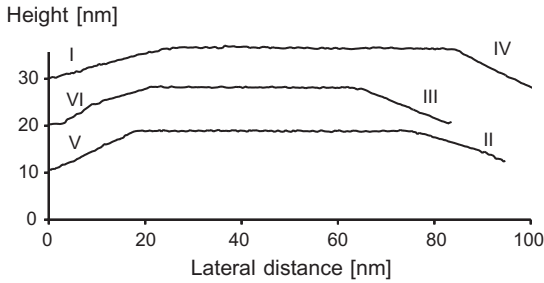


Fig. 4

Fig. 4 – Cross-sections of the grain taken perpendicular to the facets, I-IV, VI-III and V-II.

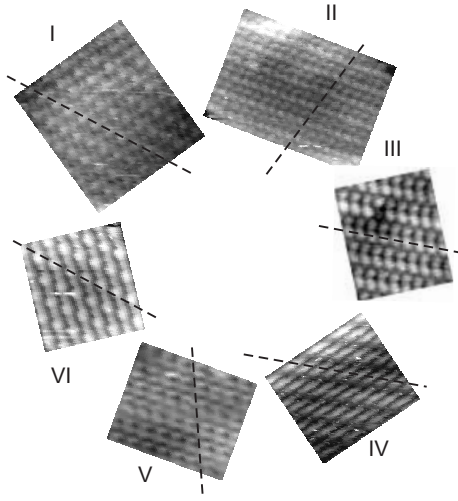


Fig. 5

Fig. 5 – STM-images resolving the molecular arrangement of the facets I to VI. No shading has been applied to avoid the accentuation of specific directions. A planar background has been subtracted individually.

stacking of subsequent layers. Since the ordering continues up to the top layer it may be assumed that the different layers have the same lattice as the top layer, which has been discussed above. If the layers were stacked without a lateral displacement between the subsequent unit cells the ordering of the facets should be described by the same lateral periodicity and angles, which is obviously not the case. To reconstruct the three-dimensional arrangement of the crystal we first consider the inclination of the facets, which can be deduced from the cross-sections displayed in fig. 4. It shows three cross-sections, which have been chosen at right angles to the borderlines I-IV, II-V and III-VI. The inclinations for the facets have been listed in table I. It should be noted that the experimental uncertainty of about  $3^\circ$ , which may be estimated by comparing different measurements, is relatively large. A first estimate on how the facets are formed may be obtained if one combines the slope with the height of a single layer. The latter has been determined by the analysis of the “staircase”, *e.g.* of facet VI to  $3.5 \pm 0.3 \text{ \AA}$  which roughly agrees with the findings for the bulk structures [17]. Assuming that one step down is associated to the addition of one unit cell in lateral direction, the slope for the facets can be calculated in the absence of a lateral displacement. For the facets I, III, IV and

TABLE I

Facet	Inclination $\gamma$ ( $^\circ$ )	$\text{tg } \gamma$
I	16	0.29
II	17	0.31
III	22	0.40
IV	27	0.51
V	26	0.49
VI	16	0.29

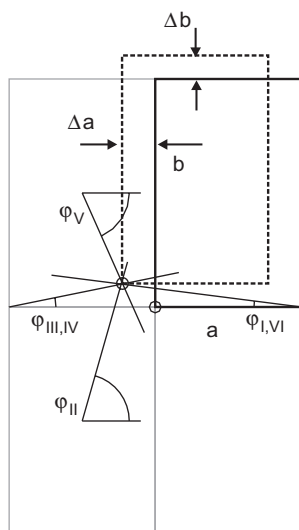


Fig. 6

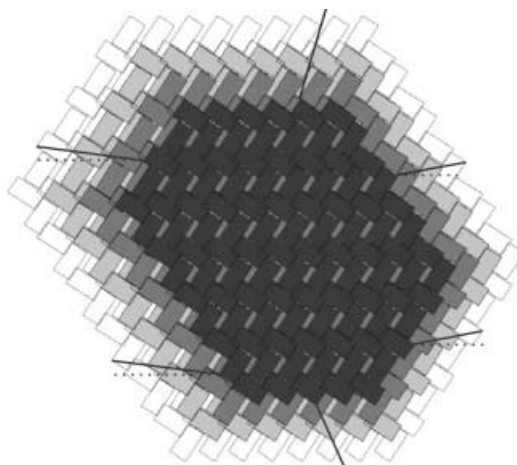


Fig. 7

Fig. 6 – Geometric construction of the displacement of adjacent layers.

Fig. 7 – Model for the arrangement of the molecules within the crystal. For simplicity, the molecules have been represented by rectangles. To explain the characteristic directions observed on the facets lines connecting the “corners” of the molecules have been drawn. The dotted lines correspond to the  $a$ -direction.

VI the distance between adjacent diagonals in the lattice has to be considered which is given by  $d = \frac{a-b}{\sqrt{a^2+b^2}} = 10.5 \text{ \AA}$ . This yields a slope of  $\text{tg } \gamma = 0.33$  which corresponds to  $\gamma = 18^\circ$ . This value is larger than the one found for I and VI and smaller than the one for III and IV. This indicates a displacement to the upper left when going downwards. Nevertheless, it remains reasonable to assume the addition of one unit cell per layer. Applying the equivalent argumentation for the facets II and V leads to a prediction, which is wrong. The addition of one unit cell perpendicular to the short axes would result in a shift of  $b = 19.5 \text{ \AA}$  or a slope of  $\text{tg } \gamma = 0.18$  or  $\gamma = 10^\circ$ . This is definitely smaller than the observed values for II and V and may not be explained by a displacement between the layers. By looking at the molecular unit cell it is suggested that only half of a unit cell is added in the  $b$  or  $-b$  direction going one step down the facets II and V, respectively. This yields  $\text{tg } \gamma = 0.36$  or  $\gamma = 20^\circ$ , which falls between the observed values. Hence, taking a displacement into account this may describe the observation.

The key to access the displacement lies in the observed “directions” in the molecular resolved images of the facets. Four (six) important directions are shown in fig. 2 and in fig. 5.

TABLE II

	Angle ( $^\circ$ )
$\varphi_{\text{I,VI}}$	7
$\varphi_{\text{II}}$	74
$\varphi_{\text{III,IV}}$	11
$\varphi_{\text{V}}$	65

TABLE III

	Å
$a$	$12.5 \pm 0.7$
$b$	$19.5 \pm 0.7$
$\Delta a$	$(- )2.8 \pm 0.5$
$\Delta b$	$2.0 \pm 0.5$
$c$ (spacing of adjacent layers)	$3.5 \pm 0.5$

The angles relative to the directions of the short axes of the unit cell are summarized in table II. Within the experimental uncertainty of about  $\pm 1^\circ$  the angles  $\varphi_I$  and  $\varphi_{VI}$  as well as  $\varphi_{III}$  and  $\varphi_{IV}$  agree. Based on these assumptions made above, the displacement may be obtained by a simple geometric construction, as has been depicted in fig. 6. The strong solid black line depicts the unit cell of the top or upper layer, the circle denotes the origin. The gray lines extend the corresponding lattice. The essential part consists in finding the starting points at which the lines corresponding to the observed directions start. On the facets the observed spacing is given by the displacement of subsequent layers plus the additional unit cell (or half of it). Since we are only interested in the displacement between subsequent layers, the effect of the additional unit cell is taken care of by shifting by one lattice vector (“folding back”) in the opposite direction. *E.g.*, for the facets III and IV one unit cell is added to the right, hence in our construction the starting point is shifted by one lattice to the left and the angle  $\varphi_{III,IV}$  defines the corresponding line. The same applies for  $\varphi_{I,VI}$  with the opposite shift. The point at which the lines intersect marks the displacement of the unit cell of the lower layer with respect to the origin of the upper. However, to achieve a reasonable accuracy the intersecting lines should be at about right angle. Furthermore, the intersections of additional lines yield an estimate of the error margin. Since for the slopes II and V only half a unit cell is added and since the second molecule is centered within the unit cell, the corresponding starting point is offset by half a lattice vector both in the  $a$ - and  $b$ -direction. In doing so, five more intersections are obtained. All of them fall in a very small region. The circle around the intersections has a radius of  $0.5 \text{ \AA}$ , which is a rather conservative estimate of the error. The displacement is  $-2.8 \text{ \AA}$  in the  $a$ -direction and  $2.0 \text{ \AA}$  in the  $b$ -direction. The dotted lines mark the position of the lower unit cell. The observed three-dimensional arrangement of the molecules, which is summarized in table III, exhibits a layered structure with a rectangular unit cell. For comparison to the observed topography of the crystallite fig. 7 shows a model representing the molecular arrangement of the facets. For the sake of simplicity, the molecules have been sketched by rectangles. If one compares the findings with the known bulk structure determined by electron diffraction [17], these layers may be identified with the [102]-plane of the  $\alpha$ - or  $\beta$ -structure. The dimension of the unit cell is close to the projection of the one of the  $\alpha$ -phase on the [102]-plane, which has  $a = 11.96 \text{ \AA}$  and  $b = 19.91 \text{ \AA}$ . However, the stacking is significantly different. In the  $\alpha$ -phase only a shift in the  $b$ -direction of  $1.9 \text{ \AA}$  and none along the  $a$ -direction is found. From previous studies of the monolayer growth [18] on the same substrate it is known that there is a strong interaction between the molecules and the substrate. Apparently, the influence of the substrate may be transferred over several layers inducing a three-dimensional structure, which differs from the bulk even for a crystal of 20 layers. It should be noted that the discussed structure is only one of several ones, which could be identified on the same sample [19]. A similar complexity of structures has been found by grazing-incidence X-ray diffraction for films of  $200 \text{ \AA}$  PTCDA on Ag(111) [20]. The advantage of the method applied in the present paper is the capability to analyze individual crystallites independently. The size of the grain may be fairly small; for the given example it is below  $100 \text{ nm}$ .

*Summary.* – If a material grows with a microcrystalline structure on a surface, the three-dimensional structure of individual grains may be identified by means of STM (or AFM) if the top layer and at least one facet may be atomically or molecularly resolved. This is demonstrated for the example of the organic molecule PTCDA on Cu(110). For the given preparation it forms truncated hexagonal pyramids with rather shallow slopes. All the facets could be molecularly resolved allowing an unambiguous identification of the molecular arrangement. The crystallite is formed by planes in which the molecules form a “herringbone structure” with rectangular unit cell. The subsequent layers are laterally offset in the direction of the short as well as in the direction of the long axis. The structure resembles the known  $\alpha$ - and  $\beta$ -structure of the bulk. However, there is a marked difference of the displacement between adjacent layers.

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