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Using atomic force microscopy to reveal the nature of extended defects in organic semiconductors: the role of crystal growth mechanisms

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Abstract. Optical and atomic force microscopy measurements on the {001} form of the organic semiconductor quaterthiophene revealed interlaced spiral patterns arising from growth layers mutually rotated by 180° about the normal to the (001) crystal face. This bulk-surface relationship, along with the height of the exposed step ledges of the order of 10-100 nm, evidences the complex polytypic nature of these crystals in which the basic $P2_1/c$ layer gives rise to several different stacking along [001], even within the same crystallite. The consequences on solid state physical properties arising from these crystal growth phenomena are briefly discussed.

1. Introduction

Since its invention in the early 1980s [1], scanning probe microscopy (SPM) has been constantly improved to become a fundamental tool for research in the field of materials science. In particular, since the very beginning inorganic semiconductors were particularly blessed by the SPM performance. More recently, an increasing interest has grown around organic molecular semiconductors and their potential applications for molecular electronics [2]. Still today, 25 years after the SPM breakthrough, the same "old" atomic force microscopy (AFM) can produce new insights about molecular materials by imaging the micro-topography of crystal surfaces. The physical properties of organic semiconductors, either as single crystals or crystalline thin films, rely on intrinsic molecular properties and packing. Therefore, care is taken to produce high quality crystalline materials. Unfortunately, even with a thorough optimization of growth techniques (physical vapour transport, vacuum sublimation, molecular beam deposition, etc) [3-5], growth mechanisms active under the selected experimental conditions can lead to formation of extended defects involving a significant part or, in the worst case, even the whole volume of the sample. Recognition of surface patterns, along with analysis of symmetry requirements necessary for such phenomena to occur [6-8], led us to find out polymorphic-polytypic transitions for a well known and promising class of organic semiconductors, oligothiophenes. Recent findings on quaterthiophene (4T) single crystals and thin films are here

discussed. Further, it is shown that spiral growth patterns observed on the 4T{001} form can be used to reveal and interpret anomalies in the stacking of molecular layers.

2. Experimental procedure

Crystals of the low temperature polymorph of 4T [9] were grown with the floating drop technique [5] and made to adhere to amorphous silica slabs prior to characterization. Thin films of tetracene and 4T on potassium hydrogen phthalate (KAP) (010) cleaved substrates were grown, under UHV conditions, by organic-MBE at a base pressure below 5×10^{-10} Torr, with a Knudsen effusion cell. A constant deposition rate of about 0.5 nm min^{-1} was maintained during film growth. AFM images were collected in Tapping™ mode, using single beam Si cantilevers (nominal force constant of 40 N/m, resonance frequency 300 kHz) with a Multimode Nanoscope IIIa AFM (Digital Instruments). Optical images were taken with an Olympus BX51 microscope using Nomarski differential interference contrast (DIC).
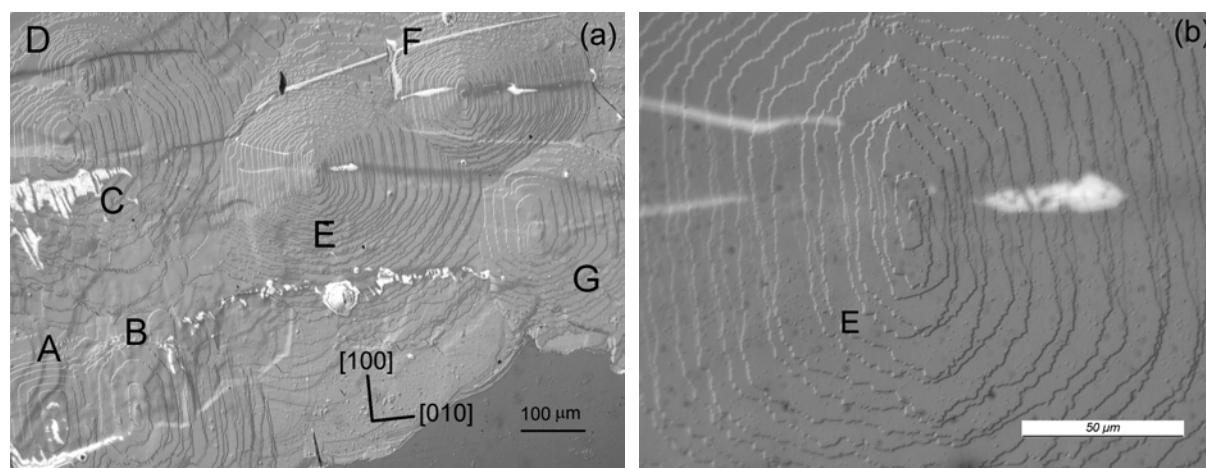

Figure 1. DIC optical microscopy images of: (a) growth hillocks centred at the outcrop of screw dislocations on a (001) face of a 4T crystal; (b) enlargement of the growth hillock marked with E, showing interlacing of steps (periodic zigzag along the [010] direction).

3. Results and discussion

Since requirements about crystal size, surface roughness and quality needed for further studies (e.g optical characterization) are not always available with classical growth techniques [4], we developed the floating drop (FD) method to grow very thin organic crystals [5]. This affords {001} lamellae of the low temperature polymorph of 4T [9] exceeding 1 cm in size, with a thickness from few hundred nanometres, suitable for optical measurements, up to few µm depending on crystallization conditions [5]. With the FD method, crystals are nucleated from the mother solution and subsequently enlarged at low supersaturation by isothermal solvent evaporation.

Under these conditions, crystals can grow by classical BCF spiral mechanism [10]. 4T single crystals obtained in such a way sometimes exhibit surface features which are the fingerprint of the growth mechanisms. Figure 1a shows a group of growth spirals with steps running parallel to <100> and <110> and covering the (001) face of a ~1 µm thick 4T crystal. All the growth spirals in figure 1 share the same in plane orientation of steps, as expected for a single crystal. However, they can not be compatible with a regular stacking of the basic monomolecular d_{002} layer along the [001] direction, as required by the space group P2$_1$/c [9]. Indeed, all spirals exhibit a characteristic steps interlacing, i.e. pairing and dissociation of step ledges, occurring twice for each turn of the spiral arms and producing a zigzag pattern that reveals an alternate A/B sequence of macrosteps. This is necessarily associated with a faulted stacking of the d_{002} layers [6-8, 11] owing to the presence of a screw dislocation determining, on the (001) surface, an exposed ledge built by two macrosteps mutually rotated by 180°.

As an example, step height measurements show that hillock E (figure 1b and 2) comprises two spirals of the same sign, generated by a single screw dislocation, and characterized by large Burgers vectors of ~18 nm and ~36 nm, corresponding to two macrosteps built by ca. 12 and 24 monomolecular layers, respectively. The resulting periodicity along [001] reaches then ~54 nm, whilst the correct $P2_1/c$ unit cell periodicity with two monomolecular layers is c = 3.05 nm [9].
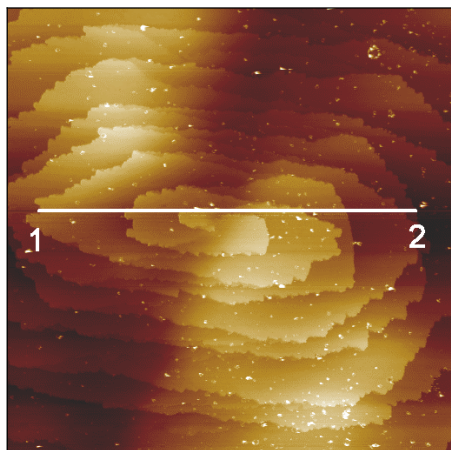

Figure 2. AFM image (73 x 73 μm^2) of spiral E with steps interlacing . The two helicoidal macrosteps A and B (see also figure 3) are self-perpetuated by growing around the screw dislocation core.
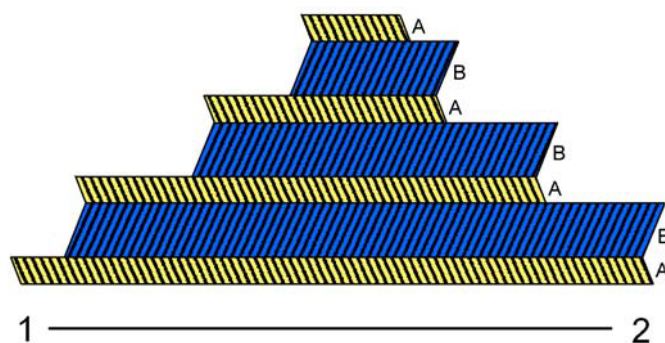

Figure 3. Schematic view of a growth hillock. Normally stacked and faulted macrosteps have, generally, different thicknesses. Due to tilting of 4T molecules with respect to the (001) plane and the 180° mutual rotation of A and B macrosteps, ledges expose re-entrant angles at the common fronts originating from step advancement anisotropy.

Interlacing of steps occurs because bunched layers (the macrosteps) belonging to the two spirals are mutually rotated by an angle $\phi = 180°$ about the normal to the (001) face. The monoclinic anisotropy in the (001) plane causes faster moving steps to catch up with the slower underlying ones to produce common fronts outside the zigzag zone. AFM data provides similar results for all growth spirals in figure 1a, each of them having its own specific height for the pair of interlaced steps generating the growth hillock (table 1). Therefore, interlacing of steps reveals that within the same "single" crystallite the growth domains generated by different dislocation sources possess different stacking of the basic d_{002} slice and, hence, different resulting unit cell c vectors and β angles.

Table 1. Thickness of interlaced growth steps exhibited by the growth hillocks in figure 1a.

Growth spiral	Thickness of layer A (nm) / number of d_{002} layers	Thickness of layer B (nm) / number of d_{002} layers
B	15 /10	55 / 36
C	30 / 20	75 / 49
E	18 / 12	36 / 24
G	12 / 8	70 / 46

All unsubstituted oligothiophenes share the same herringbone packing of molecules giving rise to 2D lamellae, e.g. the d_{002} slice of 4T [9]. Another important structural feature of 4T is the ~24° tilt angle of the long molecular axis with respect to the lamella, all molecules being tilted in the same direction when seen along [010]. Therefore, the anomalous stacking of macro-steps, each of them built

from several d_{002} lamellae piled according to the correct P2$_1$/c symmetry, represents periodic polysynthetic twinning associated with complex long period polytypism. Rotation of 180° about c^* of macro-steps with respect to the next and previous ones generates alternating layers of molecules tilted to the right or to the left when viewing the crystal down [010] direction (figure 3). Each polytype can be described by the Ramsdell notation [12] as $(p+q)$ M[(0)$_{p-1}$ 180(0)$_{q-1}$ 180] where $(p+q) \times d_{002}$ is the period of the polytype along c^*, based on p parallel monomolecular layers stacked with the same orientation (0 degrees) followed by q monomolecular layers (all with the same relative orientation) rotated by 180° with respect to the preceding and following p layers. The polytype period $(p+q)$ equals the length of the Burgers vector of the screw dislocation generating the step interlacing. M indicates the monoclinic structure of the polytype; the limiting case where $p = q$ would correspond to an orthorhombic polytype, in principle a situation accessible also for the system here discussed.

The anomalous (001) interface between adjacent macro-steps can be easily realized because the faulted orientation causes only a small loss of the inter-lamella attractive energy, estimated as ~7% through docking modelling of rotated 4T(002) layers [13]. Appearance of periodic polysynthetic twinning in lamellar systems is a phenomenon since long known [11, 14] and is related to formation of twinned nuclei (2D or 3D) on the pre-existing growing crystal face. For these nuclei, the small interface energy loss enables a significant nucleation frequency; afterwards, they can continue to grow and, thanks to the emergence of screw dislocations with large Burgers vectors, can cooperate with the correctly oriented layers originating the long period periodic polysynthetic twins.

The aforementioned structural effects, revealed at the moment in bulk crystals, can also be relevant for thin films since screw dislocations are commonly observed features due to growth conditions and substrate roughness [15]. In figure 4 the presence of active growth spirals is demonstrated for tetracene and 4T thin films grown by MBE on a KAP (010) substrate. Therefore, future analysis of the growth mechanisms of organic thin films [16] will be directed also towards detection of anomalous surface patterns indicative of stacking faults and polymorphic-polytypic modification of the basic crystal structure.
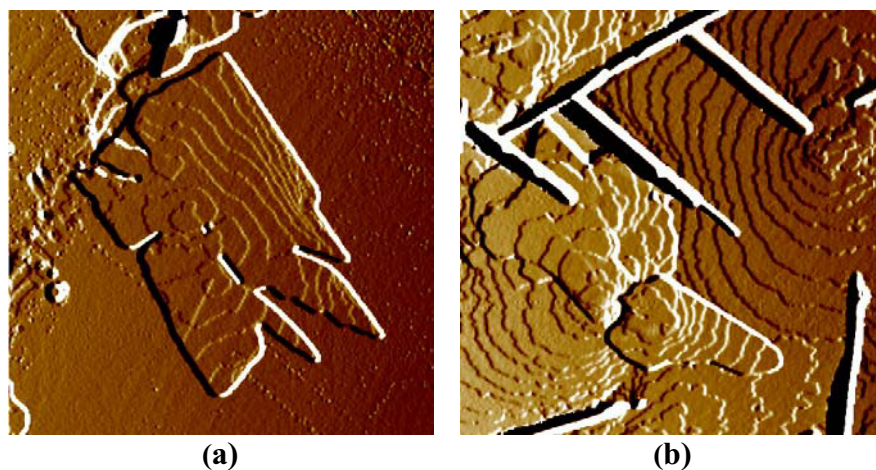

(a)   **(b)**

Figure 4. AFM error signal images of: (a) tetracene thin film (5.5 x 5.5 μm^2) and (b) 4T thin film (7 x 7 μm^2) grown on KAP(010) substrate showing several dislocation outcrops.

4. Summary

Due to the just described growth mechanisms, the crystalline material exhibits different physical properties depending on the volume of the crystal selected for the physical characterization. As an example, the optical response may vary significantly since it depends on the orientation of the transition dipole moment which, being roughly aligned with the long molecular axis, exhibits two different orientations according to the polysynthetic twinned structure [17].

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