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# Structural characterisation of ultra-high vacuum sublimated polycrystalline thin films of hexathiophene

M. Campione [a,*], A. Sassella [a], M. Moret [a], A. Thierry [b], B. Lotz [b]

[a] Department of Materials Science, Università degli Studi di Milano Bicocca, Via R. Cozzi 53, 20125 Milano, Italy
[b] Institut Charles Sadron—CNRS, 6 rue Boussingault, 67083 Strasbourg Cedex, France

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## Abstract

Hexathiophene occupies a place of relevance in the context of organic semiconductors employed as active layers in opto-electronic devices. The knowledge of the structure of this class of materials in the film-phase is crucial for understanding and tailoring the performances of these devices. Here, thin films of hexathiophene have been deposited on silica by organic molecular beam deposition under controlled growth conditions. The structure of these films has been investigated by transmission electron diffraction compelling evidences of the presence of a structure different from the bulk phase.

*Keywords:* Atomic force microscopy (AFM); Electron diffraction; Organic semiconductors; Structural properties

## 1. Introduction

Among molecular organic semiconductors, hexathiophene (6T, $C_{24}H_{14}S_6$) is definitely one of the most studied and promising in view of technological applications. Many peculiarities of this material motivate the huge amount of published papers dealing with its physical properties and performances as active layer in opto-electronic devices [1–4]. Above all, among oligothiophenes, 6T exhibits both high conjugation of π-electrons and high crystallinity in the solid state. Secondly, the relatively high molecular weight of 6T, which ensures strong intermolecular interactions, allows the layer-by-layer growth of the thin film phase on common inert substrates by deposition techniques in ultra-high vacuum [5].

The first step towards a thorough comprehension of the intrinsic physical properties of a material, such as charge transport and light absorption and emission, consists in the determination of its crystalline structure. Several structures have been determined for 6T, both from X-ray diffraction data collected from the powder [6], single crystals [7,8], and films [9] (see Table 1). Similarly to other oligothiophenes [10], in these structures 6T crystallizes in a layered structure, with molecules all parallel to one another, stacked in a herringbone fashion, and tilted to the lamellar plane. Two polymorphs of the bulk phase have been discovered (namely the low temperature, α6T/LT, and high temperature, α6T/HT, polymorphs) by growing the material from the vapour phase in the presence of a temperature gradient, then analysing crystals nucleated at different temperatures [11]. The structure determined by Porzio et al. [6] from the powder presents close similarities with the α6T/LT polymorph [7]. Finally, the only X-ray data collected on films a few micrometers thick grown at various temperatures have been reported by Servet et al. [9,12]. For the film phase, different polymorphs (α, β, γ, and δ) of 6T have been obtained by changing the substrate temperature or the deposition rate [12]. Among these polymorphs, a temptative structure has been deduced from X-ray data for describing the β phase [9], which is the one that was found in films few micrometers thick and deposited at room temperature with high deposition rate. For the other polymorphs, only the value for the interlayer spacing is provided. The α phase presents only slight differences with respect to the β phase and was obtained under the same conditions of the β phase but with low deposition rate. The γ phase obtained at 190 °C presented close

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* Corresponding author. Tel.: +39 02 64485012; fax: +39 02 64485400.
*E-mail addresses:* marcello.campione@mater.unimib.it (M. Campione), adele.sassella@mater.unimib.it (A. Sassella), massimo.moret@mater.unimib.it (M. Moret), Thierry@ics.u-strasbg.fr (A. Thierry), Lotz@ics.u-strasbg.fr (B. Lotz).

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Table 1
Unit cell parameters, tilt angle of the molecular axis to the lamellar plane normal ($\phi$), herringbone angle ($\tau$), and interlayer spacing of the known crystalline structures of 6T

| | 6T-Porzio [6] | α6T/LT [7] | α6T/HT [8] | 6T-Servet [9] |
|---|---|---|---|---|
| $a$ (Å) | 45.38 | 44.71 | 9.14 | 5.98 |
| $b$ (Å) | 7.86 | 7.85 | 5.68 | 7.80 |
| $c$ (Å) | 6.03 | 6.03 | 20.67 | 50.28 |
| $\beta$ | 99.0° | 90.76° | 98.0° | 111.3° |
| $\phi$ | 23.8° | 24.1° | 33.6° | 21.3° |
| $\tau$ | 62° | 65° | 55° | 62° |
| Interlayer spacing (Å) | $d_{(200)}=22.41$ | $d_{(200)}=22.35$ | $d_{(001)}=20.48$ | $d_{(002)}=23.42$ |

similarities with the one reported in Ref. [6]. Finally, the δ phase was obtained at 260 °C and showed a peculiar long spacing possibly deriving from a unit cell containing three monolayers of 6T.

So far, different attempts have been done in order to characterize the structure of ultrathin 6T films, both providing transmission electron diffraction (TED) data performed on films grown from the melt [13], sublimated onto carbon-coated electron-microscope grids [13], sublimated onto polytetrafluoroethylene [14], and by optical methods [15]. In all these cases, the presence of the α6T/LT polymorph was assumed for determining the orientation of the molecules within the crystalline domains, without investigating the possibility to have a low-temperature phase with a structure different from the bulk one. The knowledge of the equilibrium crystalline structure of the thin film phase and of the orientation of molecules is of fundamental importance in prevision of a description of epitaxial relations of 6T films deposited on foreign crystalline substrates. Here, 6T thin films a few nanometers thick were grown on silica substrates by organic molecular beam deposition (OMBD) under growth conditions ensuring the presence of micrometer-sized single crystalline domains, as measured by atomic force microscopy (AFM). A thorough TED analysis performed on such domains demonstrates the presence of a phase with the same structure as that reported by Servet et al. [9], with crystalline domains with molecules tilted by 68.7° to the substrate plane in competition with twinned domains with molecules orthogonal to the substrate surface.

## 2. Experimental details

6T thin films were grown by means of OMBD [16], starting from commercially available 6T microcrystalline powder in a Knudsen effusion cell at 260 °C, keeping the substrate temperature at 25 °C. The pressure in the growth chamber was kept at $8\times10^{-8}$ Pa during deposition. The film nominal thickness was monitored by means of a quartz crystal microbalance [17]. The substrates were silica plates cleaned with several solvents and dried under a nitrogen flow before mounting within the growth chamber.

AFM images were collected in intermitting contact (Tapping™) mode with a Nanoscope IIIa MMAFM (Digital Instruments) using silicon cantilevers.

For electron microscopy observation the 6T films were backed with a thin carbon film, isolated from the substrate, and transferred on copper grids. The 6T/carbon films were taken apart from the substrates by floating them on a dilute HF solution, or by using the known poly (acrylic acid) (APA) method. In the latter case, the 6T/carbon film backed by dried APA was floated on distilled water, which dissolves APA. A Philips CM12 electron microscope working at a voltage of 120 kV was used. Diffraction patterns were obtained at a spot size of 50 nm, using a condenser aperture of 50 μm and a selected-area aperture of 30 μm.

Indexation of the experimental diffraction patterns was carried out using the program Cerius2© (Accelrys) on the basis of crystal structures reported in the literature.

## 3. Results and discussion

Table 1 reports the unit cell parameters of the known crystal structures of 6T. The spacing among lamellae (interlayer spacing) is also reported in Table 1.

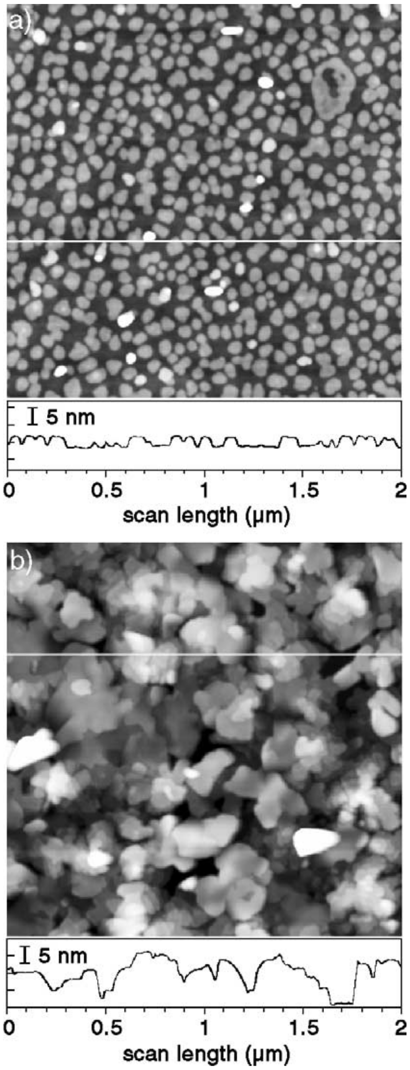

Fig. 1. $2\times2$ μm$^2$ AFM images and cross-sectional profiles along the white lines of 6T thin films grown by OMBD on silica substrate. Nominal thicknesses are (a) 0.5 nm and (b) 15 nm.