

Synchrotron X-ray investigation of tetracene thin films grown at different deposition fluxes

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Abstract

Grazing incidence synchrotron X-ray diffraction was used to investigate the structure of vacuum-sublimated tetracene thin films (6–50 nm thick) deposited on silicon dioxide. The films were found to be polycrystalline with crystallite texturing and size increasing with the deposition flux. This last parameter was found to have a great influence on the relative amounts of the polymorphs (thin film α and β phases) composing the films. These two different phases are characterised by different spacings of the (00 ℓ) planes, the spacing of the α phase being closer to that of the bulk. The thicknesses of the two phases in the film change as a function of the deposition flux. Finally, we discuss the role of the deposition flux on the charge-carrier mobility in tetracene films used as active layers in field-effect devices. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

Thin films constituted by small organic conjugated molecules are the object of intense research due to their potential use in organic (opto-) electronic devices [1–5]. In order to achieve the optimal properties of such organic devices, the control of the morphology and the structure of the films is essential [6]. It is now well established that the substrate surface coverage, the degree of crystallinity, the crystalline domain size and the texturing of the films determine device performance. These parameters are influenced, among others, by the deposition flux. Therefore, the structural study of the film growth as a function of the deposition flux is relevant to correlate the structural with the (opto-) electronic properties of the device.

Tetracene thin films grown by vacuum-sublimation were already used to fabricate field-effect transistors (FETs) with relatively high hole mobility [7] and, thanks to their reasonably high electroluminescence quantum yield [8], light-emitting field-effect transistors [9–12].

Recently, it was shown that hole mobility in tetracene thin films increases with the deposition flux [13]. This was ascribed to the uniform substrate surface coverage from the early stages of the film growth. In this work, we report a grazing incidence synchrotron X-ray diffraction (XRD) study of tetracene films, in order to gain insight into the role played by their structural features on the charge mobility, when the films are employed as active layers in FETs.

2. Experimental

Commercial tetracene powder from Tokyo Chemical Industries was vacuum-sublimated and deposited on

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oxidised silicon. The oxide was thermally grown to a thickness of 100 nm by a wet process and cleaned by O_2 . The tetracene films were deposited with nominal thicknesses (t_f) of 50 nm at fluxes (F) from 0.005 to 0.3 nm/s. X-ray diffraction measurements were carried out at the XRD1 beamline of the ELETTRA synchrotron facility (Trieste, Italy) using a monochromatic beam of 8.05 keV. The incidence angle on the sample was about 1° and a 2D CCD camera was placed normal to the incident beam direction and 130 mm from the sample to record the diffraction pattern in reflection mode. Sample and detector were kept fixed during the measurements. Thanks to the use of the 2D detector, a wide range of scattering angles was collected, which enabled simultaneously the identification of the crystalline phases and the determination of the crystallite texturing and size, together with their out-of-plane misorientation with respect to the substrate.

3. Results

In order to have a reference for the diffraction of thin films, a preliminary 2D diffraction image was recorded in transmission mode from the tetracene powder mounted in a glass capillary. The intensity integrated along the Debye rings was extracted as a function of the scattering angle. This diffraction spectrum was indexed by means of Powdercell software [14] using the crystallographic parameters and atom coordinates reported by Holmes et al. for triclinic tetracene [15]. Its unit cell contains two planar molecules tilted with respect to one another in a herringbone structure. Their long axes are parallel to each other and tilted by 22° from the normal to the (001) plane. The molecules are confined in a layer parallel to the (001) plane having a thickness of 1.226 nm, which corresponds to the (001) interplanar spacing.

Fig. 1 shows diffraction images of tetracene films grown at (a) $F = 0.005$, (b) 0.025 and (c) 0.3 nm/s. Besides a widely diffused halo due to the amorphous SiO_2 layer, Debye rings produced by the films are visible. This result confirms that tetracene forms polycrystalline films, as previously reported in the literature [7,16]. Fig. 1 shows also an inhomogeneous intensity distribution along the rings. This is related to a crystallite texturing in the films, which increases with the deposition flux. At high flux, the diffraction images show that the 00ℓ reflections are confined in a narrow region in the centre of the 2D detector, while the hkl reflections are present in the lateral ones. This indicates that the fraction of crystalline domains with average orientation of the (00 ℓ) planes parallel to the substrate increases with the flux. The narrower the widths of the intensity arcs along the Debye rings, the larger is the fraction. The film thus consists mostly of stacked (00 ℓ) planes, that theoretical calculations demonstrated to have the lowest surface energy [6]. The diffraction images are invariant after sample rotation by any angle around its normal. This implies cylindrical symmetry of the crystallite texturing with axis perpendicular to the sample.

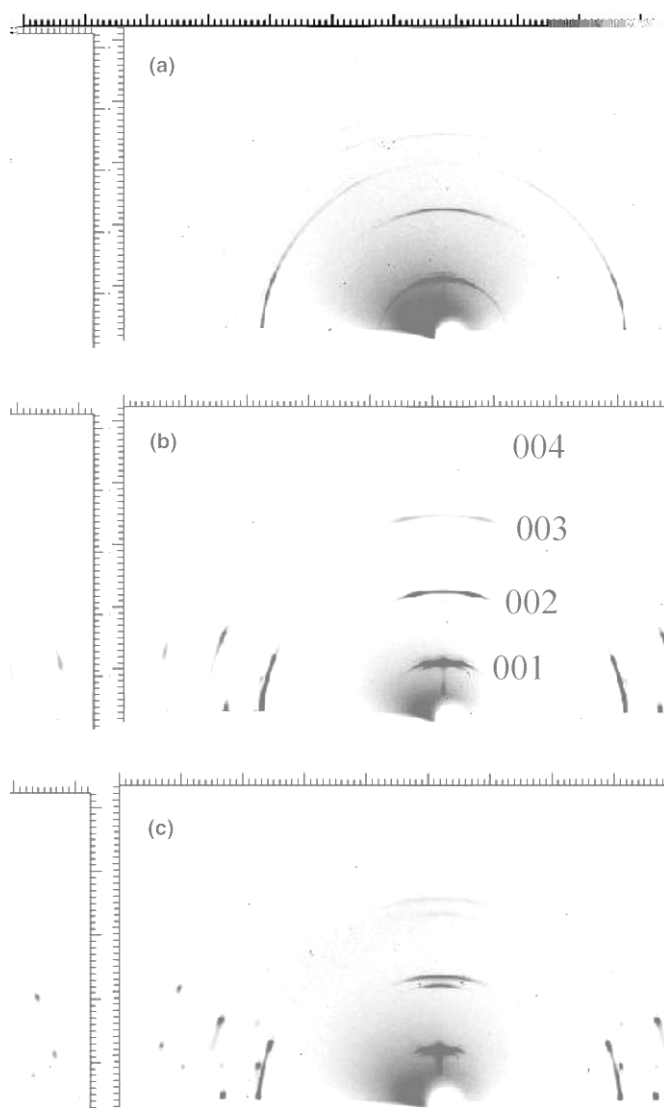


Fig. 1. Diffraction images of tetracene films grown on SiO_2 at: (a) $F = 0.005$, (b) 0.025 and (c) 0.3 nm/s. The nominal thickness of the films is 50 nm. Due to the grazing incidence geometry, only the upper part of the diffraction pattern reaches the detector.

Diffraction spectra obtained from the tetracene powder and the film deposited at $F = 0.025$ nm/s are compared in Fig. 2. For the film, the figure shows the integrated intensity along the Debye rings in the central region of the 2D diffracted image. Attention was paid particularly to this region because, as will be evident below, it was able to provide information on the depth distribution of the structural characteristics of the films.

The shift towards low scattering angles observed for the film peaks compared to those of the powder indicates an increase in the d_{hkl} interplanar spacing in the film. In particular, the d_{001} distance increases from 1.226 ± 0.005 nm (powder) to 1.240 ± 0.005 nm (film). This polymorph will be referred to in the following as the thin film α phase. Beside the α phase, a second polymorph is present, characterised by a larger interplanar spacing, $d_{001} = 1.320 \pm 0.005$ nm. This polymorph will be referred to in

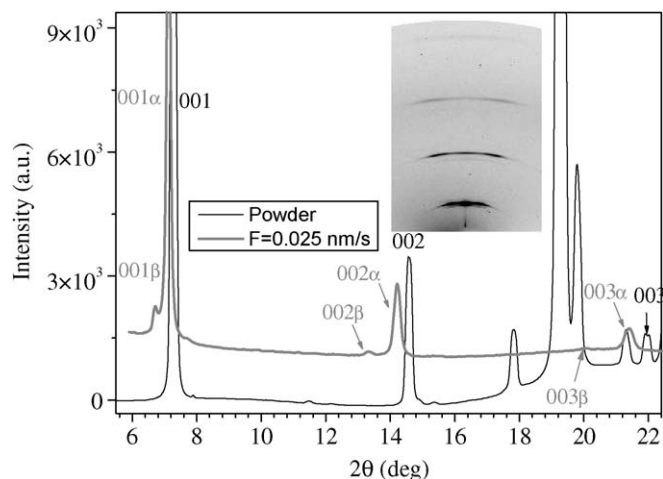


Fig. 2. Diffraction spectra of a 50 nm thick tetracene film deposited at $F = 0.01$ nm/s (bold line) and of the tetracene powder used as the reference standard (thin line). Inset: diffracted image recorded in the central region of the 2D detector.

the following as the thin film β phase. The simultaneous presence of two polymorphs in tetracene films is observed for the first time. The β phase forms in thin films grown with $F > 0.01$ nm/s (Fig. 1(b) and (c)). We will discuss the relevance of the finding of two polymorphs in the next section, in which the structural characteristics of the tetracene thin films will be related to the hole mobility of FET devices.

In both polymorphs, the long molecular axis is near to the normal to the substrate, as expected for isotropic and inert substrates, where the interaction between molecules is stronger than between molecules and substrate [17]. The two polymorphs are characterised by different orientations of the tetracene molecules: in the β phase, the tilt angle of the molecular axis from the normal to the surface is smaller than that in the α phase [18].

Fig. 1 also shows that, even when the β phase forms, there is no splitting of the $hkl \neq 00l$ reflections, each of them indeed giving only one diffraction spot (Fig. 1(b) and (c)). The impossibility of identifying the hkl reflections in the diffraction spectra can be interpreted assuming that the atomic disorder parallel to the film in the β phase is so strong that its lateral reflections are too weak to be seen.

The relative amounts of the two phases were evaluated by the ratio $I_\beta/(I_\alpha + I_\beta)$, where $I_{\alpha,\beta}$ are the areas of the 001 peaks obtained by intensity integration of the Debye rings. This evaluation was done as a function of F (Fig. 3). For $F = 0.005$ nm/s, the β phase is hardly observable (Fig. 1(a)) and the ratio $I_\beta/(I_\alpha + I_\beta) \sim 0$, while an increase to about 70% is evident at $F = 0.2$ nm/s. Beyond this value, the ratio drops to about 30%.

In the case of the pentacene [19] it has been shown that the most expanded phase grows in contact with the substrate; in the following we will assume that this is true also for the present case of tetracene on silicon dioxide. With this assumption, the crystalline particles of the two

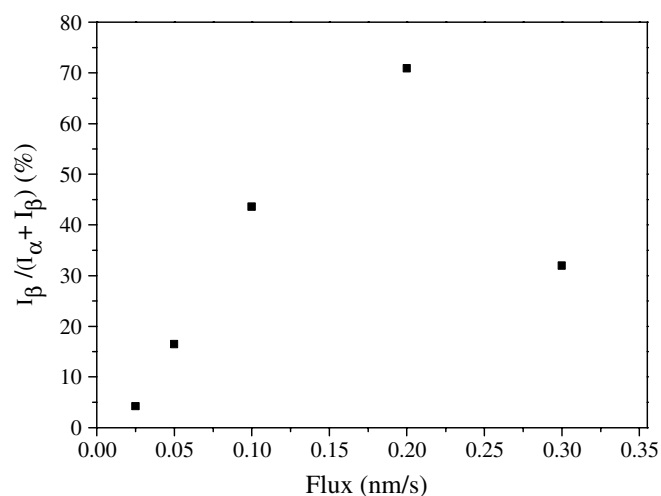


Fig. 3. Percentage of the diffracted intensity diffracted by the β phase as a function of the deposition flux for film thickness of 50 nm.

Table 1

Deposition fluxes (F), percentages of the β phase in the film (β phase (%)), thicknesses of the β phase (t_β), thicknesses of the α phase (t_α) for film thickness of 50 nm

F (nm/s) $\pm 10\%$	β phase (%) $\pm 10\%$	t_β (nm) $\pm 10\%$	t_α (nm) $\pm 10\%$
0.025	4.2	2.1	47.9
0.05	16.5	8.3	41.7
0.100	43.6	21.8	28.2
0.200	70.9	35.5	14.5
0.300	31.9	16.0	34.0

polymorphs are not randomly distributed in the film. This enabled the relative fractions of the tetracene phases to be converted to layer thicknesses t_β and t_α . Table 1 shows these values for 0.01 nm/s $\leq F \leq 0.3$ nm/s in 50 nm thick films. t_β grows up to 35 nm at $F = 0.2$ nm/s, after which thinning of the β phase layer and thickening of α phase layer are observed.

The diffraction patterns allowed also the evaluation of the crystalline domain size at the different deposition fluxes. The sizes normal to the surface were calculated by Scherrer's equation [20] from the full widths at half maximum of the $00l$ reflections measured across the Debye rings. In the α and β phases they increase with the flux. The hkl reflections of the α phase, unlike the $00l$ reflections, are spotty for high F . This indicates that the crystallite dimension is strongly anisotropic, with the lateral size greater than the vertical one. The spotty appearance of the hkl reflections means tendency towards a single crystalline structure, which prevents the evaluation by the Scherrer's equation of the domain size parallel to the surface. In these cases, a size estimate of several micrometers can only be done [20].

4. Discussion

One of the most relevant results of this work is the observation of the simultaneous presence of two polymorphs in tetracene thin films, both exhibiting interplanar

spacings $d_{00\ell}$ larger than those of the powder. Their relative amounts are strongly dependent on the deposition flux.

When the films are grown at low $F \leq 0.025$ nm/s, i.e. in conditions close to the equilibrium, they contain almost only the α phase (see Fig. 1(a) and (b) and Table 1). This is the more thermodynamically stable phase, because its lattice parameters are very close to those of the powder. Increasing F above 0.025 nm/s leads to the formation of consistent amounts of the β polymorph, with t_β growing almost linearly with F up to $F \leq 0.25$ nm/s.

The formation of the more deformed (less stable) β phase is induced by the interaction of the molecules with the substrate. Though smaller than that among molecules in the film, this interaction is not negligible, as demonstrated by the good adhesion of the film on the substrate. This phenomenon is effective at the beginning of the film growth and the t_β values is ~ 2 nm for $F = 0.025$ nm/s (Table 1).

When the flux is greater than 0.025 nm/s, the contribution of the β phase to the 50 nm film thickness increases. This can be explained by considering that, once the influence of the substrate on the nucleation and growth of the β phase vanishes, the incoming molecules do not have enough time to accommodate themselves in a low energy state (i.e. the nucleation of the α phase) so that the film grows by thickening of the β phase. Therefore, an increase in t_β is favoured by a faster film growth.

For $F > 0.2$ nm/s, a sharp decrease in t_β is observed. This reversed behaviour could be related to the stress relieve occurring when a certain t_β has been overcome.

The increase in the deposition flux strongly influences the film texturing and the crystallite size. In fact, it induces an enhancement of the crystallite orientation parallel to the surface. At the same time, the lateral domain size attains a value as large as several micrometers.

It has been reported that a high deposition flux determines an increase in FET mobility [13]. This phenomenon has been attributed to the improved substrate surface coverage, thanks to a 2D rather than a 3D film nucleation [21]. The present results suggest two further factors which might influence hole transport in tetracene films, i.e. the formation of the thin film β phase and the increase in the crystalline domain sizes. Indeed, (i) the higher tilting of the molecular axis towards the surface normal in the β phase determines a more favourable orientation of the molecules for hole transport across the transistor channel [3,22] and (ii) the increased crystalline domains size leads to a reduction in the number of crystalline domains boundaries that can act as traps for charge carriers [23,24].

5. Conclusions

In summary, thanks to the use of X-ray synchrotron radiation we could study the crystallographic properties of thin tetracene films grown at room temperature on silicon dioxide substrates as a function of the deposition

flux. Tetracene films showed a polycrystalline structure with crystallite texture and size increasing with increasing deposition flux. Two thin films phases (α and β) were identified: they show different (00ℓ) interplanar spacings and different orientations of the tetracene molecules. The β phase, characterised by a larger distance, grows above a flux threshold. The phase with interplanar spacing closer to that of the powder (α phase) is prevalently formed at low F , though it also forms at high F by stress relaxation occurring above a threshold thickness of β phase. Both the formation of the β phase, with a more favourable orientation of the tetracene molecules, and the increase in the lateral size of the crystallite domains contribute to explain the beneficial effect of the deposition flux on the hole mobility in tetracene thin film-based FET devices.

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