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Structural characterisation of polycrystalline α,ω-dihexyl quaterthiophene thin films by transmission electron microscopy

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Abstract

α,ω-dihexyl quaterthiophene thin films have been deposited by ultra-high vacuum sublimation on silica and potassium hydrogen phthalate substrates. The influence of the substrate on the structure of the films are investigated by transmission electron microscopy and the results are compared with the morphological and optical properties of the same samples.

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1. Introduction

The employment of alkyl-substituted oligothiophenes as the active organic layer of field effect transistors has been demonstrated to give important advantages in terms of easier processability of the material and enhanced performances of the devices [1–8]. Since molecular order is a fundamental requirement whenever a high carrier mobility is requested, the growth of the active layer is a crucial step in the fabrication of the device. The formation of a thin solid film with large highly crystalline areas is not a simple task for most deposition techniques, for the morphology and structure of the organic layer can hardly be controlled during growth. The recent development of sophisticated growth techniques, such as organic molecular beam deposition (OMBD) [9], has allowed the growth of organic thin films with controlled morphological and structural properties. The present work focuses on α,ω-dihexyl quaterthiophene (α,ω-DH4T) thin films grown by OMBD on silica and potassium hydrogen phthalate (KAP) substrates. Previous studies have shown the promising performances of electronic devices made of this material and some efforts

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have been made in order to characterized the structure of thin films grown kinetically from the vapor phase [1,5]. Nonetheless, the single crystal structure of α,ω-DH4T is still unknown. Here, transmission electron microscopy (TEM) is employed to investigate the structural modification induced by the different nature of the substrates adopted. Silica, besides being an amorphous substrate, exhibits a weak interaction with most organic molecules. For this reason, thin films grown on this substrate exhibit typically an isotropic behavior [10]. On the other hand, KAP is able to induce the epitaxial growth of organic materials thanks to the possibility to obtain molecularly flat (0 1 0) surfaces by mechanical cleavage. Electron diffraction measurements performed on the grown films are compared with the results of absorption with polarized light and some indications on the film structure are deduced and discussed.

2. Experimental

α,ω-DH4T thin films were grown by means of OMBD, starting from α,ω-DH4T microcrystalline powder [11] in a Knudsen effusion cell at 190 °C, keeping the substrate temperature at 25 °C. The pressure in the growth chamber was kept at 8×10^{-8} Pa during deposition. The film nominal thickness was monitored by means of a quartz oscillator and was set to 10 nm. The substrates adopted were silica and freshly cleaved KAP(0 1 0). KAP is an organic crystal with orthorhombic structure and lattice constants $a = 9.60$ Å, $b = 13.33$ Å and $c = 6.46$ Å [12].

For electron microscopy observation the α,ω-DH4T films were backed with a thin carbon film, isolated from the substrate and transferred on copper grids. Different methods were used to take the α,ω-DH4T/carbon films apart from the substrates. For silica, the α,ω-DH4T/carbon system was floated on a dilute HF solution, or the known poly (acrylic acid) (APA) method was used. In the latter case, the α,ω-DH4T/carbon film backed by dried APA was floated on distilled water, which dissolves APA. For KAP, the substrate is just dissolved on distilled water. 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.

3. Results and discussion

α,ω-DH4T thin films grown on silica exhibit island morphology for a wide rage of thicknesses [13]. Fig. 1(a) reports a magnified TEM bright field image of a 10 nm thick α,ω-DH4T film grown on silica. Flat crystalline islands appear with dark contrast, whereas the bright background represents the amorphous carbon film deposited during sample preparation. The selected area diffraction performed on single islands with the electron beam at normal incidence on the film surface gives rise

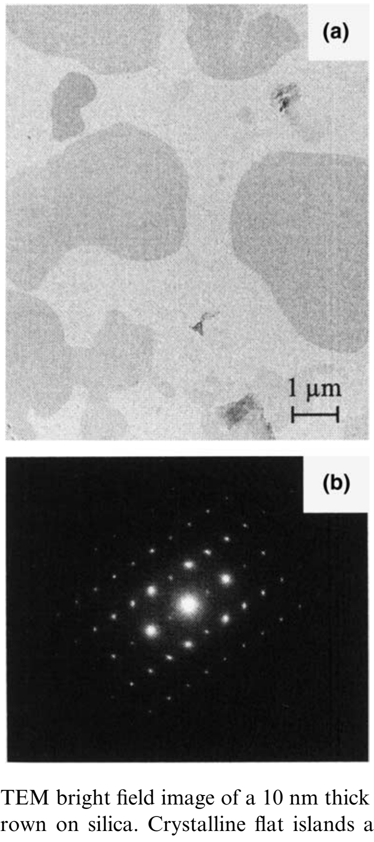

Fig. 1. (a) TEM bright field image of a 10 nm thick α,ω-DH4T thin film grown on silica. Crystalline flat islands appear with dark contrast, whereas the bright background represents the amorphous carbon film. (b) Electron diffraction pattern generated by a single crystalline island with the electron beam perpendicular to the island surface.

to the pattern shown in Fig. 1(b). This pattern allows to define a rectangular lattice of dimensions 6.06 Å × 8.16 Å. These results are in close agreement with those obtained by Katz et al. [1] on α,ω DH4T thin films grown on SiO_2/Si(0 0 1) at 100 °C. Previous studies have shown that the optical absorption spectra at normal incidence on α,ω-DH4T thin films grown on silica are independent on light polarisation direction [10]. These results are consistent with the film morphology and structure. Each island is a single crystal, but these single crystals are randomly oriented in the contact plane.

When KAP substrates are used, the interaction between the deposited molecules and the substrate surface is enhanced. From a morphological point of view, the templating effect of the crystalline substrate on the growth of α,ω-DH4T is reflected by the presence of oriented crystalline needles on the film surface. Fig. 2(a) represents an electron microscopy bright field image of a film of α,ω-DH4T grown on KAP. The oriented lines appearing with dark contrast are the needles observed also in atomic force microscope (AFM) images [13]. The brighter background in Fig. 2(a) represents flat crystalline islands, exhibiting a layered structure with spacing 29 ± 2 Å [13]. Optical absorption spectra of α,ω-DH4T thin films grown on KAP [13] show the maximum intensity of the main absorption peak with light polarised parallel to the KAP *c*-axis, and the minimum value (but not null) when it is orthogonal. Assuming the electronic transition originating the peak in the absorption spectra to be polarised along the main axis of the conjugated core [14], the experimental data indicate that the projection on the substrate surface of the molecular axis of most α,ω-DH4T molecules is parallel to the KAP *c*-axis. These data indicate a preferential but not absolute orientation of the α,ω-DH4T molecules with respect to the underlying KAP lattice. The diffraction pattern of a small selected area of a α,ω-DH4T film grown on KAP is reported in Fig. 2(b). It shows again a two dimensional rectangular pattern as the one observed for films on silica. Contrary to silica substrates, we observe essentially a unique orientation of this pattern in the plane. This suggests an epitaxial interaction between α,ω-DH4T and KAP. We must also mention that some diffraction patterns taken on large zones of the films (without selected area aperture) showed arced spots; this indicates that the orientation of few crystallites deviates from the main orientation, the observed angular deviation being less than 10°. The crystalline structure of KAP is well-known [12]. KAP is a sandwich type structure in which a core layer with ionic character consisting of $-COO^-K^+$ moieties is embedded between two phenyl layers. The van der Waals interactions between the phenyl layers are significantly weaker than the ionic interactions in the core of the sandwich. The easy $(ac)_{KAP}$ cleavage plane of the substrate is thus lined up with phenyl rings stacked along *a* and *c* which form a 2D rectangular pattern (Fig. 3(a)). As far as we are aware, the crystalline structure of α,ω-DH4T has not been solved. Thus, to analyse the relations between α,ω-DH4T and KAP we have to model the structure of α,ω-DH4T. The model is made with a graphic station operated with Cerius 42 from Accelerys. It is built up by analogy with the structure of 4T determined at low temperature

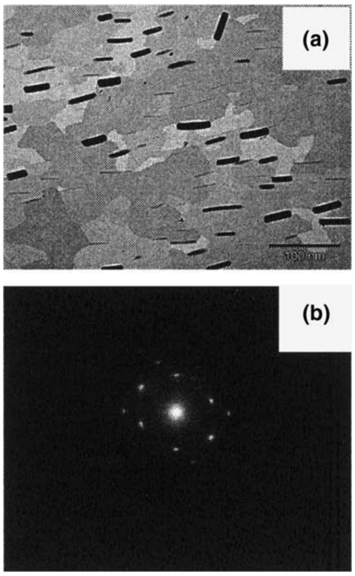

Fig. 2. (a) Bright field TEM image taken on a 10 nm thick α,ω-DH4T thin film grown on KAP (scale bar 100 nm). Oriented crystallites appear with dark contrast. The brighter background represents coalesced flat islands. (b) Electron diffraction pattern generated by a small selected area of α,ω-DH4T film on KAP.

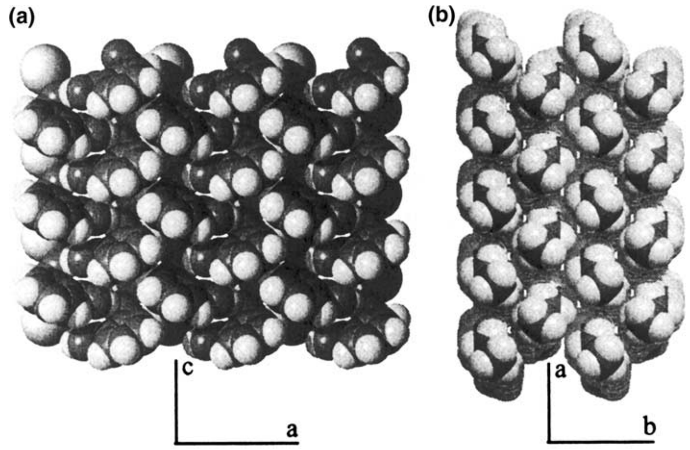

Fig. 3. Organisation of the exposed end groups in the contact planes (a) top of KAP phenyl groups and (b) CH_3–CH_2– of α,ω-DH4T.

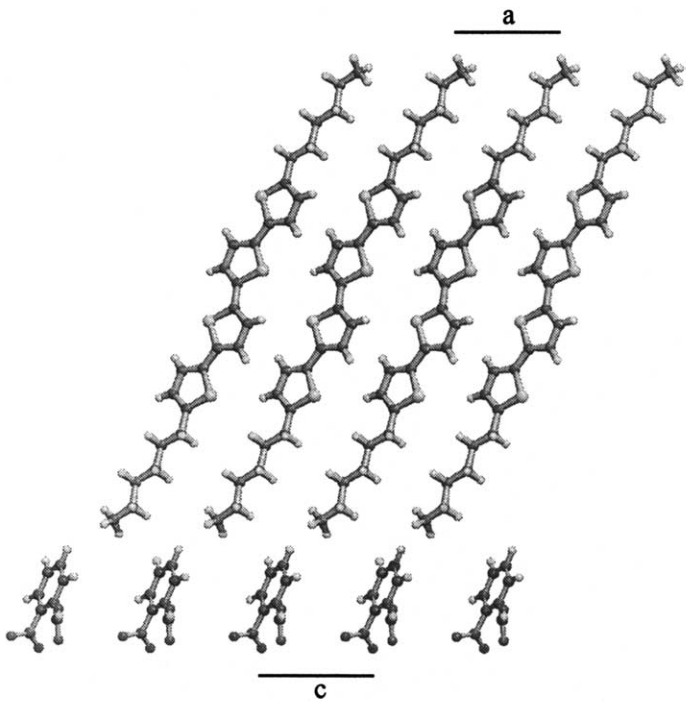

Fig. 4. Orientation of α,ω-DH4T molecules on KAP substrate viewed parallel to the contact plane.

by Siegrist et al. [15] and α,ω-dihexyl sexithiophene [6]. The starting cell parameters for *a* and *b* correspond to that determined by the two dimensional pattern observed by us and Katz et al. [1], the *c* parameter is taken as twice the height of the terraces determined by AFM [13]. The total energy competing to the primitive structure built with four molecules per unit cell was minimised using Compass intermolecular potential with no constraints for the spatial symmetry of the system.

The contact planes *ac* for KAP and *ab* for α,ω-DH4T are lined up with prominent ends of the molecules (aromatic rings for KAP, methyl end of the paraffin for α,ω-DH4T). In these contact planes we can consider the following geometrical epitaxial relations: *a* α,ω-DH4T//*c* KAP and *b* α,ω-DH4T//*a* KAP, the mismatches are 6.2% and 15%, respectively. 15% is the upper limit for the universally accepted epitaxial rules. Thus, the rigid central core of the α,ω-DH4T molecules will be parallel to *c* KAP and the methyl groups at the end of the hexyl tails of α,ω-DH4T will be in contact with the rows of aromatic rings of KAP. Figs. 3 and 4 show the organisation of the calculated position of the end groups for the planes $(0\,0\,1)_{\alpha,\omega\text{-DH4T}}$, and $(0\,1\,0)_{\text{KAP}}$ viewed along directions perpendicular and parallel to the contact planes, respectively. The inferred epitaxial relation is consistent with the maximum absorption observed in optical spectroscopy [13].

A topological relation between prominent rows of molecules along directions $\langle 1\,1\,0\rangle$ for α,ω-DH4T and $\langle 1\,0\,1\rangle$ for KAP cannot be ruled out. Topological rules of selections have already been described for polyolefins [16]. The detailed discussion of this topological case is postponed until the crystalline structure of α,ω-DH4T films is determined. We just briefly mention here that a twinning can happen in this case. This twinning will induce an orientation of the molecules non-parallel to *c* KAP, consistent with the residual absorption observed at 90°.

4. Conclusions

The structural properties of α,ω-DH4T thin films grown on silica and KAP substrates by OMBD have been explored using TEM. Both substrates have been shown to induce the aggregation of deposited molecules in crystalline islands with a densely packed structure with molecules tilted to the substrate, typical of other oligothiophenes. Islands grown on silica have been demonstrated to be randomly oriented in the contact plane, whereas islands grown on KAP have been shown to exhibit a preferred orientation. This observation analysed with the proposed model is consistent with the optical measurements performed on films on KAP.

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