



# Control of growth and charge transport properties of quaterthiophene thin films via hexyl chain substitutions

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## Abstract

Growth mechanism of quaterthiophene based organic thin films deposited by high vacuum deposition on Si:H(100) and SiO<sub>2</sub> substrates have been investigated. Especially the influence of hexyl chain end-substitutions on the growth process and the electronic transport properties of organic thin films were studied in details. Highly crystalline films were obtained for both quaterthiophene (4T) and  $\alpha$ ,  $\omega$ -hexyl-quaterthiophene (DH4T) based thin films. While unsubstituted 4T shows a typical island growth, an almost perfect layer-to-layer growth was found in the case of DH4T based films. It could be demonstrated that the change in the growth mode is directly related to the molecule structure, i.e. to the presence of hexyl chain substitutions on the 4T core, and leads to an increase of the grain size of one order of magnitude under the same evaporation conditions in the case of DH4T films. The characterization of the charge transport properties of thin films based on both molecules reveals one order of magnitude higher mobilities for the DH4T molecules. By using a simple model for charge transport in polycrystalline materials a linear dependence of the mobility on the grain size, independently from the molecule substitution, could be demonstrated. The results underline the importance of the control of the film morphology and give an impressive example of such a control in the case of hexyl end-substitutions of quaterthiophene.

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## 1. Introduction

After the demonstration of efficient organic semiconductor based field-effect transistors (FETs) [1–4] many experimental studies have shown the

strong impact of the morphology of the organic thin film on the device performances [5,6]. Defects, like grain boundaries and disorder inside the grains, present limiting factors for the mobility and the diffusion length of the charge carriers. In order to improve the charge carrier transport in organic thin films, the control of the morphology towards highly crystalline thin films is necessary. In general the morphology of an organic film depends directly on the chemical structure of the molecules, which controls the interaction between the molecules. The formation of a highly crystalline or a totally amorphous film depends, whether there is strong  $\pi$ -stacking or not between the molecules respectively, independently of other growth controlling parameters like the substrate and its temperature. Therefore one possibility to control the morphology of organic thin films is to adapt the chemical structure of the molecules. The understanding of the influence of the molecule structure on the growth of organic thin films presents an important step to higher device performances and is the subject of this present study.

In a previous work [7] the influence of the substrate, especially the substrate roughness, on the morphology of quaterthiophene (4T) films was investigated. We focused in the present work on the influence of the molecule structure on the growth process as well as on the electronic properties of quaterthiophene based thin films. The growth of the organic thin films was studied by atomic force microscopy (AFM). Very thin 4T films (2–20 nm) were investigated to determine the growth mechanism while thicker film were produced to study the influence of the substrate temperature on the film morphology.

In order to eliminate the effect of surface roughness H-passivated Si(100) and SiO<sub>2</sub> substrates were chosen which present relevant substrates for future electronic applications as well as substrates with different surface energies due to their hydrophilic and hydrophobic characters, respectively. Additionally to an earlier study [8] we present in the work a detailed correlation between film morphology, polarized absorption spectra and charge carrier mobility of 4T thin films, while by adapting a simple model of charge transport in polycrystalline semiconductors a linear depen-

dence of the mobility on the grain size could be quantified.

## 2. Experimental details

The synthesis and purification of oligomers shown in Fig. 1 have been described previously [4]. After purification, 4T and DH4T appeared as a yellow and yellow-brown powders with melting points of 179 and 208 °C, respectively.

The study of the growth mechanism and the morphology of the organic films were done on n-Si(100) ( $\rho = 0.008 \Omega \text{cm}^{-1}$ ) and SiO<sub>2</sub> substrates purchased from A.C.M. (France). The organic thin films were prepared by high vacuum evaporation at  $1 \times 10^{-6}$  mbar in an Edwards Auto 306 evaporator. Prior to the transfer to the high vacuum chamber the Si samples were etched in a 3% HF solution for 20 s which removes the natural SiO<sub>2</sub> from the surface and leads to a passivation of the surface (Si:H). The RMS roughness of Si:H and SiO<sub>2</sub> substrates were measured by AFM over a surface of 400 nm<sup>2</sup> to 1 and 4 Å respectively. The film thickness and evaporation rate were monitored by a quartz film thickness monitor (Edwards FTM6). Temperature dependence of the film morphology was performed at different substrate temperatures ( $T_{\text{sub}}$ ) between 25 and 80 °C. The deposition rate varied from 1 to 10 nm/min, while the thickness ranged from 3 to 250 nm. The characterization of the film morphologies has been done by atomic force microscopy (AFM) measurement in air with a Nanoscope III Multimode (Instrument, Inc.), operating in tapping mode. UV-Vis spectroscopy was performed on films deposited on quartz substrates with a Varian Cary

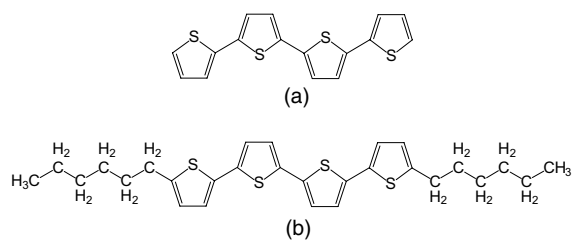


Fig. 1. Chemical structure of (a) quaterthiophene (4T) and (b)  $\alpha, \omega$ -dihexyl-quaterthiophene (DH4T).

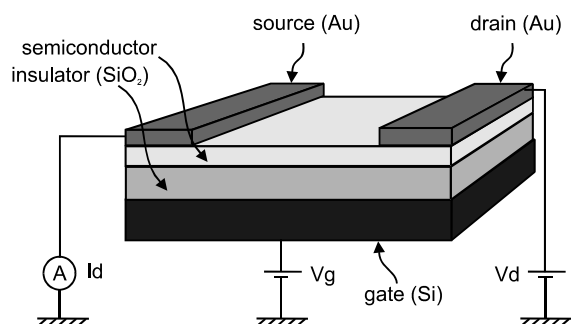


Fig. 2. Schematic diagram of the organic field-effect transistors (FET) with gate electrode and insulator layer based on highly doped Si and SiO<sub>2</sub>, respectively.

100 spectrophotometer equipped with a Varian polarizer.

Organic field-effect transistors (FET) were produced on highly doped silicon wafers covered with thermally grown silicon oxide (SiO<sub>2</sub>) purchased from A.C.M. (France). The highly doped silicon served as the gate electrode. A schema of the organic FETs used in this study is represented in Fig. 2. The capacitance of SiO<sub>2</sub> insulating layers was 13 nF/cm<sup>2</sup>. Series of organic FETs (around 100 devices in total) were produced with 4T and DH4T films deposited on SiO<sub>2</sub> substrates at different substrate temperatures (25, 45 and 80 °C). The thickness of the organic thin films used in FETs varied from 60 to 250 nm. The Au source and drain electrodes (channel length 50 μm, channel width 1 mm) were evaporated on top of the organic film through a shadow mask. Current–voltage characteristics were carried out with a Hewlett-Packard 4140B pico-amperemeter-DC voltage source.

### 3. Results and discussion

#### 3.1. Optical properties

The polycrystalline thin films of 4T and DH4T molecules were examined by UV–Vis spectroscopy. The insert of the Fig. 3 shows the normalized absorption spectra at normal incidence of 4T and DH4T films vacuum deposited on quartz substrates at  $T_{\text{sub}} = 80$  °C. Both spectra show almost

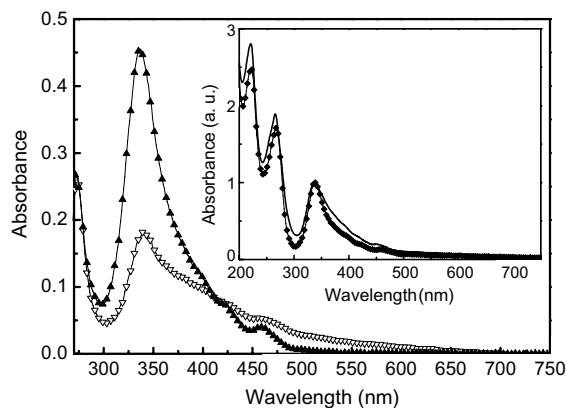


Fig. 3. Absorption spectra of a DH4T thin film (thickness 100 nm) vacuum deposited on quartz substrate at  $T_{\text{sub}} = 80$  °C under oblique incidence (60°), light being polarized parallel (—▲—) and perpendicular (—▽—) to the incidence plane. Insert: Normalized absorption spectra under normal incidence of 4T (—) and DH4T (—◆—) films vacuum deposited on quartz substrate at  $T_{\text{sub}} = 80$  °C.

identical features revealing ground and excited states of the 4T core not being influenced by the hexyl chain end-substitutions. The existence of organized thin films can be further shown by measuring the UV–Visible absorption under polarized light as already described for films based on the oligothiophene family [4,8]. In Fig. 3 the absorption spectra under polarized light at oblique incidence (60°) of a DH4T thin film (thickness 100 nm) vacuum deposited on quartz substrate at  $T_{\text{sub}} = 80$  °C is shown as an example. A dichroic ratio of 2.5 and 1.5 was obtained for DH4T and 4T thin films respectively, the higher intensity arising from the film with polarization direction parallel to the incidence plane. This confirms that the molecules are preferentially oriented perpendicular to the substrate with a higher degree of ordering in the DH4T films.

#### 3.2. Growth of unsubstituted quaterthiophene (4T) on Si:H and SiO<sub>2</sub>

In Figs. 4(a) and (b) the morphology of 4T films (nominal thickness 5 nm) evaporated on Si:H and SiO<sub>2</sub>, respectively, at  $T_{\text{sub}} = 25$  °C are shown. Both 4T film surfaces consist of separate islands with dendrite shapes and an average height of 8–10 nm,

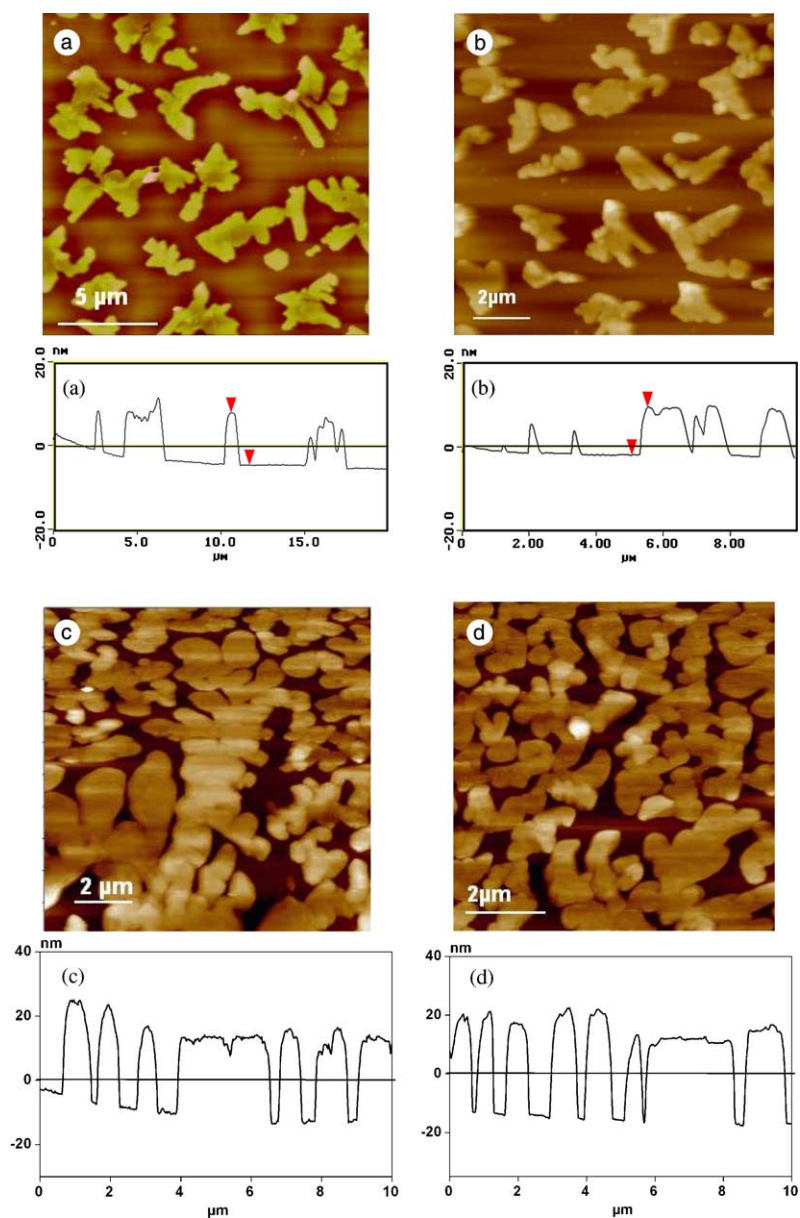


Fig. 4. AFM images and corresponding AFM profiles of 4T thin films grown by vacuum evaporation at  $T_{\text{sub}} = 25^\circ\text{C}$  on Si:H (a, c) and  $\text{SiO}_2$  (b, d); nominal film thickness 5 nm (a, b) and 20 nm (c, d).

as can be seen in the corresponding AFM profiles shown in Figs. 4(a) and (b). Even at higher film thickness of nominal 20 nm, still separated islands are observed, but their number and size are increased (Figs. 4(c) and (d)) and the corresponding AFM profiles give an average height of 25 nm.

Thus on both Si:H and  $\text{SiO}_2$  substrates, 4T films give clear evidence of island growth mode (Volmer Weber growth mode). The results are in contrast to growth studies of 4T on cleaved potassium acid phthalate (KAP) surface where due to strong molecule–substrate interactions epitaxial growth

with a layer-plus-island mode was found [9]. Comparison of the size and distribution of island on both Si:H and SiO<sub>2</sub> reveals smaller islands with higher density on SiO<sub>2</sub> indicating higher nucleation rates on the hydrophilic substrate. Furthermore we investigated the influence of the substrate temperature on the film morphology. Fig. 5 shows microcrystalline 4T thin films grown on Si:H deposited at 25 °C (Fig. 5(a)) and 80 °C (Fig. 5(b)). The AFM images indicate that increase of substrate temperature leads to larger grain with a more homogenous distribution in size and height. The maximum average grain size obtained for 4T thin films on Si:H and SiO<sub>2</sub> were 7–9 μm. The cross-section analysis on terraces present on the 4T grains show an average step size of 1.5 nm which corresponds to the length of the longest molecule axis revealing an orientation of the 4T molecules

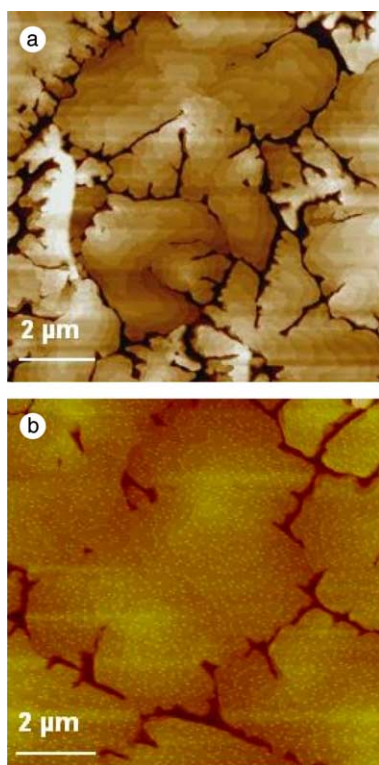


Fig. 5. AFM images of 4T film grown by vacuum evaporation on Si:H at  $T_{\text{sub}} = 25$  °C with a thickness of 150 nm (a) and at  $T_{\text{sub}} = 80$  °C with a thickness of 250 nm (b).

perpendicular to the surface of Si:H and SiO<sub>2</sub> substrates. The presence of 4T terraces on the grains reveals the crystalline organization of the film already at room temperature.

### 3.3. Growth of $\alpha,\omega$ -dihexyl substituted quaterthiophene (DH4T) on Si:H and SiO<sub>2</sub>

In Figs. 6(a) and (b) DH4T films of nominal 3 nm thickness deposited at 80 °C on Si:H and SiO<sub>2</sub> are shown. Both images demonstrate an almost complete covering of the substrate surface by the first DH4T monolayer (ML) as well as the very early state of the second ML formation. The AFM images in Figs. 6(c) and (d) show the successive formation of the second and the third ML of DH4T on SiO<sub>2</sub>, which is demonstrated in the corresponding AFM profiles in Fig. 6(e). Thus we find clear evidence of layer-to-layer growth mode (Frank Van-der-Merve growth mode) for DH4T films grown on Si:H and SiO<sub>2</sub> substrates. The average step size of the molecular terraces was determined to 2.9 nm indicating the orientation of the DH4T molecules perpendicular to the substrate plane. This average terrace height is comparable to the value found on DH4T film deposited on KAP [9], however DH4T shows layer-and-island growth mode on such KAP substrates as it was already mentioned in the case of 4T films.

Furthermore the influence of the substrate temperature on the morphology of DH4T films was investigated. Fig. 7(a) shows a DH4T film of nominal 3 nm thickness deposited at 25 °C on Si:H. At low temperature the first layer is formed by small coalescent islands indicating reduced diffusion mobility of the DH4T molecules on the substrate, however the growth mechanism is identical to that found at a substrate temperature of 80 °C. When thickness was increased to 100 nm while the substrate temperature was kept at 25 °C, the morphology of the DH4T film consists of small grains of 1–2 μm showing molecular layers with a low degree of crystalline organization as shown in Fig. 7(b). At an intermediate substrate temperature of 45 °C DH4T films consist of highly ordered domains, but many defect orientations of the

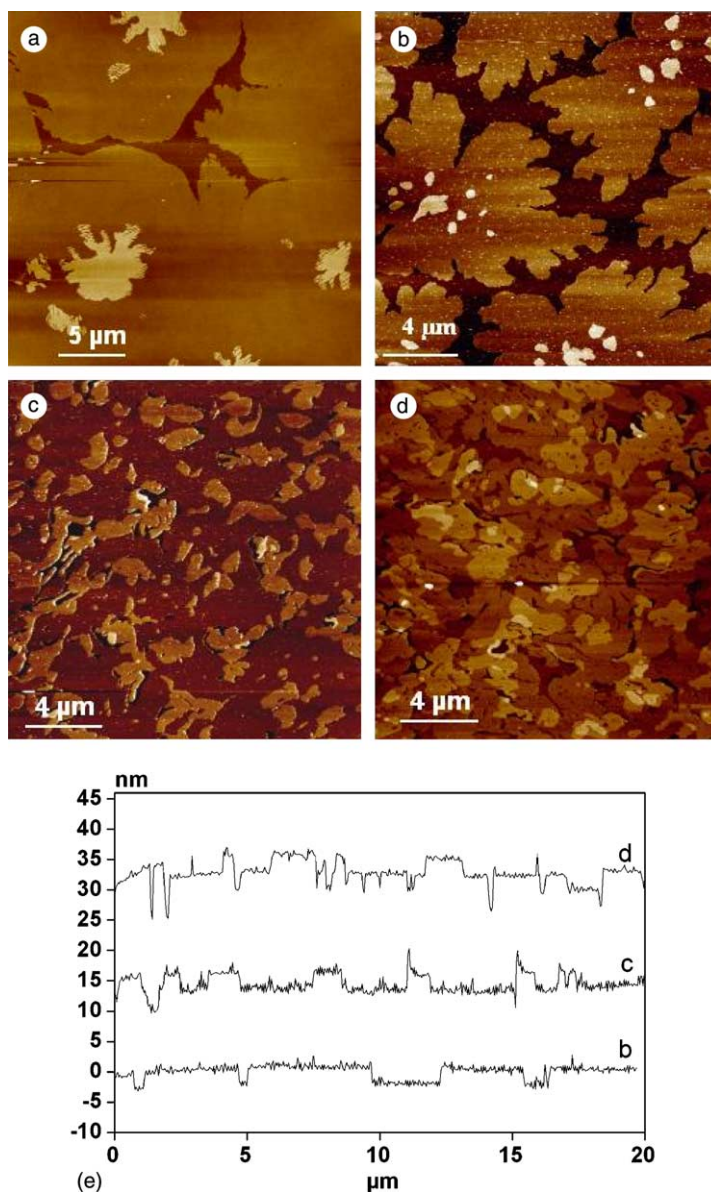


Fig. 6. AFM images of DH4T thin films grown by vacuum evaporation on Si:H (a) and SiO<sub>2</sub> (b–d) at  $T_{\text{sub}} = 80$  °C with a nominal thickness of 3 nm (a, b), 5 nm (c) and 8 nm (d); (e) corresponding AFM profiles to (b–d).

molecular layers perpendicular to the substrate still exist which limit the effective grains size to 3–4 μm (Fig. 7(c)). Only at a high substrate temperature of 80 °C highly crystalline films consisting of very large grains of an average size of 50 μm and a very low number of crystallographic defects are

obtained revealing the strong impact of the substrate temperature on the film morphology (Fig. 7(d)). We also observed large cracks across the DH4T films like shown in Fig. 7(d) which are probably result of contraction of the film during cooling as already mentioned in the literature [10].

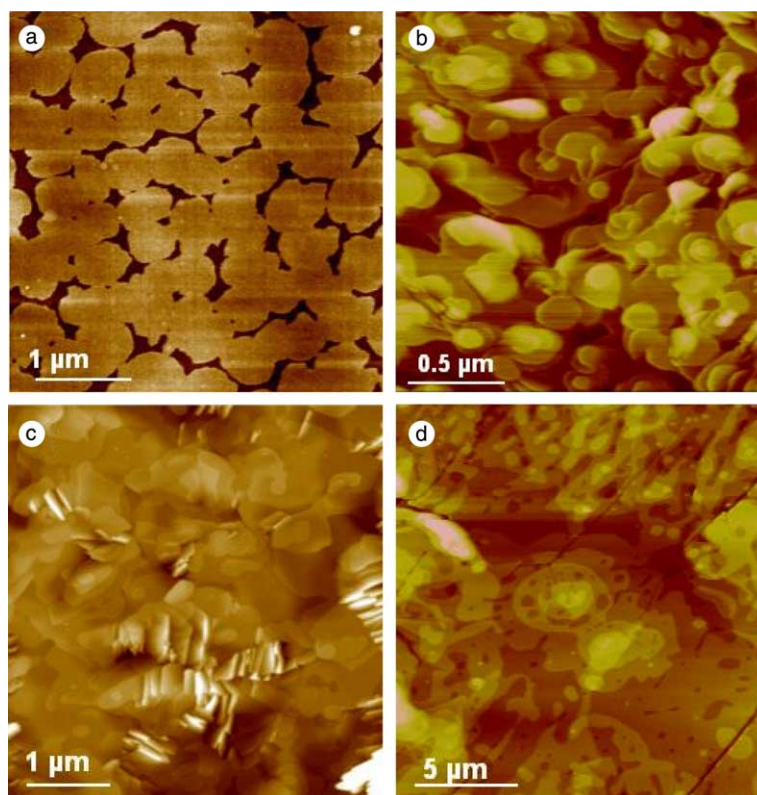


Fig. 7. AFM images of DH4T thin films grown by vacuum evaporation on Si:H at different substrate temperatures: (a)  $T_{\text{sub}} = 25\text{ }^{\circ}\text{C}$  thickness 3 nm, (b)  $T_{\text{sub}} = 25\text{ }^{\circ}\text{C}$  thickness 100 nm (c)  $T_{\text{sub}} = 45\text{ }^{\circ}\text{C}$  thickness 100 nm, (d)  $T_{\text{sub}} = 80\text{ }^{\circ}\text{C}$  thickness 100 nm.

#### 3.4. Growth of 4T on a DH4T monolayer

In Sections 3.2 and 3.3 the growth mechanism of 4T and DH4T films on Si:H and SiO<sub>2</sub> substrates was studied, respectively. We could demonstrate that a change in growth mode occurred when hexyl chains are chemically substituted to the quaterthiophene core. However in order to verify that the growth mode is directly related to the molecular structure, the interaction between the inorganic substrate (Si:H and SiO<sub>2</sub>) and the molecules always present has to be suppressed. In order to eliminate substrate influences a DH4T monolayer was first deposited on Si:H at  $T_{\text{sub}} = 80\text{ }^{\circ}\text{C}$  covering completely the Si:H substrates as shown before in Section 3.3. The AFM image in Fig. 8 shows a 4T film (nominal thickness 5 nm) deposited on a such DH4T monolayer at 25 °C. The morphology of the 4T film is quasi-identical to those found for

4T films directly grown on Si:H and SiO<sub>2</sub> substrates as shown before in Figs. 4(a) and (b). The AFM cross section in Fig. 8(b) shows clearly isolated 4T islands as well as a step size of 2.9 nm corresponding to the DH4T monolayer on the substrate (flashes). Thus the result gives the direct proof that the growth mechanism of 4T films is directly related to the molecular structure independently from the substrate.

#### 3.5. Field-effect mobility

The electrical properties of both unsubstituted quaterthiophene (4T) and  $\alpha,\omega$ -hexyl-quaterthiophene (DH4T) thin films were determined from FET measurements. Fig. 9 shows a typical electrical characteristic  $I_d = f(V_d)$  of a FET consisting of a DH4T thin film as active layer deposited on SiO<sub>2</sub> using a channel length of 50  $\mu\text{m}$ . The device

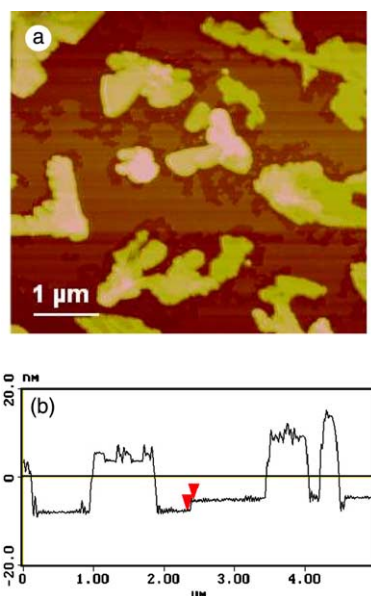


Fig. 8. AFM image of a 4T thin film (thickness 5 nm) grown by vacuum deposition at  $T_{\text{sub}} = 25^\circ\text{C}$  on a DH4T monolayer deposited before on Si(100) at  $T_{\text{sub}} = 80^\circ\text{C}$ : (a) top view and (b) the corresponding cross-section analysis.

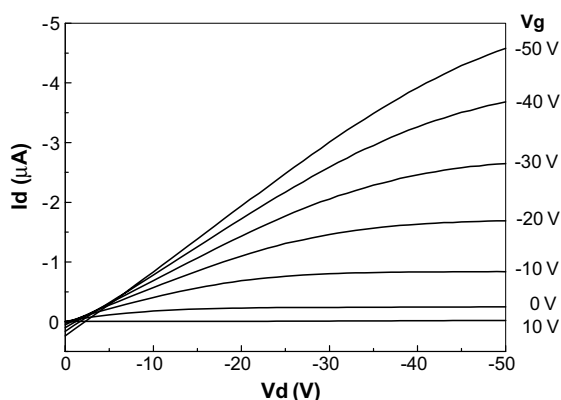


Fig. 9. Drain current ( $I_d$ )–drain voltage ( $V_d$ ) characteristics at different gate voltage ( $V_g$ ) of a field-effect transistor based on DH4T vacuum deposited at  $T_{\text{sub}} = 80^\circ\text{C}$  on  $\text{SiO}_2$ .

works in the accumulation mode with the presence of a well-defined linear regime at  $V_d < V_g$  followed by a saturation regime at  $V_d > V_g$  for a given negative gate voltage  $V_g$ . The accumulated charges are holes, so both organic layers used in the devices behaved as p-type semiconductors.

At low  $V_d$ ,  $I_d$  increases linearly with  $V_d$  and can be modeled approximately by

$$I_d = \frac{ZC_i}{L} \mu \left( V_g - V_t - \frac{V_d}{2} \right) V_d, \quad (1)$$

where  $\mu$  is the field-effect mobility,  $Z$  and  $L$  are the conduction channel width and length, respectively,  $C_i$  is the capacitance of the insulating layer per unit area,  $V_g$  the gate voltage and  $V_t$  the threshold voltage. The width to length ratio  $Z/L$  was 20/1.

In the linear regime the transconductance  $g_m$  is given by

$$g_m = \left( \frac{dI_d}{dV_g} \right)_{V_d} = \frac{Z}{L} C_i \mu V_d. \quad (2)$$

By plotting  $I_d$  versus  $V_g$  at constant  $V_d$  and equating the value of the slope of this plot to  $g_m$ ,  $\mu$  can be calculated.

For  $V_d > V_g$ ,  $I_d$  tends to saturate (saturation regime) and can be modeled by

$$I_{d,\text{sat}} = \frac{Z}{2L} \mu C_i (V_g - V_t)^2, \quad (3)$$

where  $I_{d,\text{sat}}$  is the drain current at saturation. In the saturation regime  $\mu$  can be calculated from the slope of the plot of  $|I_d|^{1/2}$  versus  $V_g$ .

Charge carrier mobilities of 4T and DH4T films were calculated by using Eqs. (2) and (3) and summarized in Table 1 for different substrate temperatures. At  $25^\circ\text{C}$  film deposition similar mobility values of  $1.5\text{--}2.7 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $1.2\text{--}4 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for 4T and DH4T films, respectively, were obtained. However at a deposition temperature of  $80^\circ\text{C}$  a difference of one order

Table 1

Variation of the hole mobility ( $\mu$ ) and drain current value ( $I_d$ ) at  $V_g = V_d = -50 \text{ V}$  of 4T and DH4T thin film transistors as a function of the substrate temperatures ( $T_{\text{sub}}$ ) during organic vacuum deposition

Oligomer	$T_{\text{sub}}$ ( $^\circ\text{C}$ )	$\mu$ ( $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ )	$I_d$ at $V_g = V_d = -50 \text{ V}$
4T	25	$1.5\text{--}2.710^{-3}$	–105 nA
	80	$5.5\text{--}8.3 \times 10^{-3}$	–276 nA
DH4T	25	$1.2\text{--}4 \times 10^{-3}$	–0.28 $\mu\text{A}$
	45	$2.1\text{--}5.2 \times 10^{-3}$	–0.48 $\mu\text{A}$
	80	$1.7\text{--}2.4 \times 10^{-2}$	–4.50 $\mu\text{A}$



of magnitude in the mobility was found resulting in a value of  $5.5\text{--}8.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for 4T films on the one side and  $1.7\text{--}2.4 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for DH4T films on the other side. All mobility values obtained are in good agreement with literature, where comparable values were determined by pulse-radiolysis time-resolved microwave conductivity (PR-TRMC) and thin film transistor studies [4,11].

In order to correlate the differences in the mobility of 4T and DH4T films to their morphology the size of the grains of the films deposited on  $\text{SiO}_2$  was determined by AFM. The maximal grain sizes of the microcrystalline films were determined to 6–8  $\mu\text{m}$  and 80–100  $\mu\text{m}$  for 4T and DH4T respectively, which correspond to the difference of one order of magnitude obtained for the mobility values of the organic thin films. At an intermediate deposition temperature of 45 °C DH4T films show grains of 4–5  $\mu\text{m}$  with mobility values of  $2.1\text{--}5.2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . In order to obtain more quantitative results a simple model for the charge transport in polycrystalline films considering the influence of defects at grain boundaries is discussed [12,13]. In the model, the mid-gap states, associated with the grain boundary, are introduced (Fig. 10). These states create a sheet of charge associated with the occupancy of the states inducing electrostatically a barrier layer within the surrounded material. Independently of the nature of the boundary states (donor or acceptor states) the region around the boundary is invariably depleted. Thus the charge transport in polycrystalline films is given by both the charge mobility inside the crystalline grains and in the

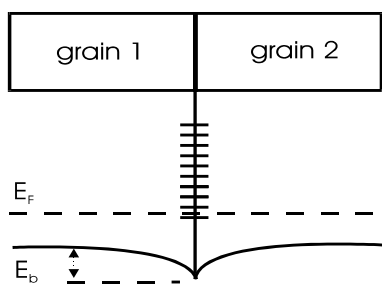


Fig. 10. Schematic drawing of the valence band at a grain boundary in a polycrystalline organic semiconductor (p-type).

grain boundaries. The effective mobility of the material can be written as the harmonic mean of the mobility in each region [12]:

$$\frac{1}{\mu} = \frac{1}{\mu_G} + \frac{1}{\mu_{GB}}, \quad (4)$$

where  $\mu_G$  and  $\mu_{GB}$  are the mobility in the grains and in the grain boundaries, respectively. If all defects are located at the grain boundaries, the assumption  $\mu_G \gg \mu_{GB}$  can be done and the effective mobility equals to that in the grain boundary. According to the barrier formation the current flowing through a grain boundary at room temperature is limited by thermoionic emission. For polycrystalline films with grain sizes larger than the Debye length  $L_D$ , the mobility can be modeled by [13]

$$\mu = \mu_{GB} = \frac{q\bar{v}l}{8kT} \exp\left(-\frac{E_b}{kT}\right), \quad (5)$$

where  $\bar{v}$  represents the electron mean velocity,  $l$  the magnitude of the grain size,  $k$  the Boltzmann constant,  $T$  the absolute temperature,  $q$  the electronic charge and  $E_b$  the barrier height. According to Eq. (4) the mobility should increase linearly with the grain size. In Fig. 11 the mobility values of the 4T and DH4T films measured in the presented FETs are plotted as a function of the observed grain size. An average grain size of 25  $\mu\text{m}$  in

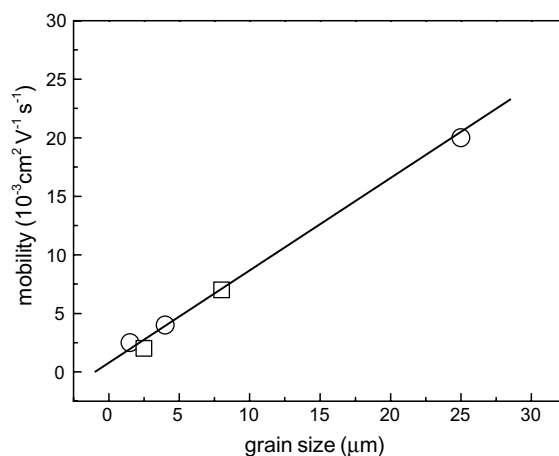


Fig. 11. Plot of the field-effect mobility  $\mu$  versus grain size for 4T ( $\square$ ) and DH4T (O) thin films.

the case of DH4T deposited at  $T_{\text{sub}} = 80$  °C was taken which corresponds to the half value of the channel length of the FET. The result shows that the mobility values of 4T and DH4T films can be described as a function of grain size following Eq. (5) indicating that charge transport in 4T and DH4T based thin films is given by the 4T core as well as by the grain size, but not influenced by the hexyl substitutions.

#### 4. Conclusion

The influence of the molecule structure on the growth mechanism of organic semiconductor thin films has been investigated. The growth studies on quaterthiophene (4T) based molecules give clear evidence that growth mode is directly given by the molecule structure. While 4T shows island growth mode, an end-substitution of hexyl chains on the 4T core leads to a modification of the growth mechanism to a layer-by-layer growth mode. The change in growth mode results in increase of grain size of one order of magnitude in the case of DH4T films. Furthermore we demonstrate that grain size and crystalline organization are strongly controlled by substrate temperature during the film evaporation. The obtained charge carrier mobility values in the 4T and DH4T films with different morphologies controlled by the substrate temperature show good agreement with a simple model of charge transport in polycrystalline materials predicting linear dependence of the mobility on grain size. The results reveal high charge transport given by the 4T core in both 4T and DH4T thin films, while especially grain size presents the limiting factor. Finally end-substitution of hexyl chains on the quaterthiophene core is an example of direct control of growth mechanism of organic semiconductor by chemical engineering

leading to improved charge transport in the organic thin films. While the presented work is an example of growth control via effect of hexyl end-substitutions on quaterthiophene, the influence of the molecule rigidity and planarity on the growth behavior of oligothiophene based block-oligomers will be reported elsewhere [14].

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