Oligothiophene field effect transistors of DDnT and DPnT type: Morphology, performance in vacuum and in air

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Abstract

Field effect transistors were prepared by vacuum sublimation of the oligothiophenes DDnT and DPnT. Their electrical performance was investigated in vacuum ("in situ") and after exposure to air ("ex situ"). Their morphology was compared with that of end capped oligothiophenes, ECnT, and the influence of the number of monomer units and of the chain-end molecules was studied.

The in situ as well as ex situ drain current-voltage characteristics exhibit linear and saturation regions, however, with a large drain current increase after exposure to air due to oxygen doping. A change in layer thickness from 10 to 120 nm resulted in only a small drain current change in vacuum indicating that most of the OFET conduction takes place near the interface with the gate insulator (SiO₂). In situ values for threshold voltage, field effect mobility, transconductance, and carrier density are reported. The carrier density increases by a factor of 10 after exposure to air. The highest field effect mobility ($4.8 \times 10^{-3} \text{ cm}^2/\text{Vs}$) was observed for DP5T, which had the lowest carrier concentration. The influence of the gate voltage on the transconductance is discussed.

I. Introduction

Organic field effect transistors (OFETs) have received increasing attention in recent years because of their widespread flexibility of chemical structure and functionalization, at basically low cost [1]. Possibilities of integration on flexible plastic substrates point toward a development of “plastic electronics” [2].

Polythiophenes [1] and their corresponding α -conjugated oligomers [3,4] appear to be of particular interest because of their excellent electrical and transport properties, their environmental stability, and their OFET performance [5]. Molecular systems with different chain lengths can be achieved e.g in the case of end-capped oligothiophenes (ECnT) with $n= 3$ to 8 (Fig.1a) [6]. In this case, α, α coupled thiophene monomers are terminated by cyclohexane cap molecules to stop further polymerization leading to a defined chain length. As theoretically predicted [13], they exhibit in optical investigations a regular increase of the HOMO-LUMO separation with inverse chain length [7-12].

Also the charge transfer properties correlate with inverse chain length [14,15]. But the performance of OFETs depends not only on chain length but also on other experimental conditions like purity, structural order, film thickness, morphology, electrodes, etc. [16-18]. High field effect mobilities have been reached by optimizing the experimental conditions [19]. A mobility increase with chain length, the role of purity, and the possible influence of molecular self-assembly as suggested in the case of α -8T [20] still needs further investigation.

In general, the best mobility values were obtained for vacuum deposited oligothiophenes, where structural ordering has been suggested at low deposition rates ($< 1 \text{ \AA/s}$) [21].

In this paper, OFETs from different oligothiophenes, namely of the type DDnT and DPnT (see DP4T, DD4T, DP5T, DD6T, and TD8T depicted in Fig. 1b) were prepared by vacuum deposition. The aim of the present study is to report, for the first time, “in situ” (i.e. under vacuum conditions), as compared with the performance “ex situ” (after exposure to air), the investigation of the above OFET systems. Data on their transconductance and mobility values for different chain length are presented.

II. Experimental

The synthesized [22] and investigated oligothiophenes for the OFET systems are depicted in fig.1b. They are 3,3'''-dipentyl--quaterthiophene (DP4T), 5,5'''-didodecyl- quaterthiophene (DD4T), 3,3'''- dipentyl--quinquethiophene (DP5T), 5,5'''-didodecyl--sexithiophene (DD6T), and 3,3'''-3''',4'''-tertadidodecyl--octithiophene (TD8T). These systems differ in chain length, and as well as in the nature of the chain end molecules. The chain ends were C_5H_{11} in the case of DPnT oligothiophenes and $C_{12}H_{25}$ and TD8T molecules in the case of DDnT [22].

Thin layers (10 –500 nm thickness) were prepared by vacuum sublimation at very low deposition rates of $< 1 \text{ \AA/s}$ in a system using a basis pressure of 2×10^{-9} mbar [11]. The system had three vacuum chambers with a manipulator in the main chamber which could turn the sample by rotation into the molecular beam [11]. The sample holder was provided with four electrical connections for in situ electrical characterization.. Si/SiO₂, occasionally ITO, and glass were used as substrates. The substrate temperature was controlled, and the film thickness was monitored *in situ* by a vibrating quartz monitor during evaporation. Independently, the layer thickness was controlled externally by means of ellipsometry, Tolanski interference and Dektak measurements. The pressure applied during the

sublimation /evaporation process varied between 6×10^{-8} and 5×10^{-7} mbar. The temperature of the evaporation oven was controlled by a Cr/CrNi thermocouple. The sublimation temperatures, T_{sub} , are given in Table I:

As expected, these temperatures are correlated with the number of thiophene monomers.

For OFETs, the oligomer layers were deposited on n⁺-Si /SiO₂ substrates where the n⁺ Si with an Al contact served as a gate electrode, the SiO₂ layer with a typical thickness of 400-500 nm was employed as a gate insulator.

The source and drain contacts were prepared by evaporation of 200 nm thick Au layers before vacuum sublimation of the oligothiophenes. They were structured by optical or e-beam lithography. Their typical length was 2mm, and the source drain distances were 20 μm , 10 μm , 5 μm , and 2 μm . This resulted in enhancement or depletion mode thin film transistors (TFT) with low off-current. For comparison of the electrical properties a standard source drain distance of 20 μm was chosen. The contacted chip was attached by silver paste to a chip carrier, introduced through a vacuum lock into the vacuum system with subsequent evaporation of the oligothiophene layers. In this manner the transistor was ready to perform “in situ” measurements under vacuum conditions.

III. Results and Discussion

III.1 Morphology

The morphology of the layers made with the oligomers shown in Fig. 1b was examined by “ex situ” scanning electron microscopy (SEM) and compared with the morphology of

endcapped oligothiophenes (ECnT). All layers exhibit a polycrystalline particle structure [23,24].

In the case of end-capped oligothiophenes, ECnT, the particle dimensions gradually decrease with increasing number of monomer units n (see Table 2). In this case one may think that when n is small the bulky chain ends impede longitudinal particle growth. However when n increases, needle-like morphology is formed. Furthermore the bulky end-groups impede a good chain packing and the particle size is reduced when n increases.

On the other hand, for the oligomers of the type DDnT and DPnT, the morphology is different from that of ECnT. This is probably due to the influence of different chain-end molecules. An example of the influence of the molecular structure on the morphology for systems having the same number of monomers and prepared under identical conditions (change from EC4T to DD4T and EC6T to DD6T), is shown in Fig.2 [24]. Table 2 gives a summary of the measured crystallite sizes [23,24].

DDNT molecules with small ends yield needle-like polycrystalline particles with a particle length 10 times larger than the width ($r=10$). With increasing molecular size the particle length increases while the particle width gradually decreases ($r=95$). This suggests that lateral molecular coherence decreases with chain length while the chain-end packing improves leading to longer needle particles.

As a tendency, with increasing the number of monomers of the chain, a finer and more homogeneous morphology of the polycrystalline particles is obtained. The highest homogeneity is observed for DP5T and DP6T, owing probably to the smaller size of the chain-end molecules (C_5H_{11}) or to their different position within the molecule(see Fig.1b).

In summary, the number of monomer units and the size and position of side chains have a pronounced influence on the structure /morphology of the vacuum sublimated layers and, as a consequence, also on the electrical and OFET properties.

III.2. Electrical OFET characteristics: Drain current –voltage dependence

All transistors investigated in this chapter are enhancement mode p-channel TFTs.

For the channel length of 20 μm , which was chosen for comparing the electrical characteristics of different transistors, short channel effects [1,25,26] should be neglected. Therefore the common long channel approximation for the dependence of the drain current, I_D , on the source –drain voltage U_D [27,28] should be expected:

$$I_D = (C_i \mu_{\text{FET}} W/L) [(U_T - U_G) + U_D^2/2] \quad (1)$$

where W is the width and L the length of the channel, C_i the gate insulator capacitance per unit area, U_T the threshold voltage, and U_G the gate voltage.

The I_D - U_D characteristics should exhibit a linear region at low voltages and a saturation region at high voltages, as reported for previous OFET work [1,19]. This is demonstrated in Fig 3 where *in situ* measurements for DP5T transistors of two different layer thicknesses, namely 10 nm and 120 nm, are shown. The measurements were done during evaporation in vacuum.

Note that U_D voltages are very high, up to 100 V, gate voltages U_G were varied in 20 V steps from –80 V downward. All measurements were performed in the dark. Also, it is noteworthy that when the thickness is increased from 10 to 120 nm only a relatively small

current increase is observed (by about a factor of 2.5). This means that the majority of carriers responsible for the drain current are generated in the thin layer near the interface.

Fig. 4 shows an *ex situ* measurement of the same transistor after exposure to air for 30 min. The drain current, I_D , has increased by one order of magnitude relative to the *in situ* value. This is expected due to the oxygen doping upon exposure to air. More remarkable is that the shape of the I_D - U_D characteristics is nearly the same as that for the in-situ measurement. The characteristic seems to be shifted simply by one order of magnitude to higher currents. The results of Figures 3 and 4 refer to DDP5T that had the smoothest surface morphology and the highest field effect mobility (see Table 3).

Qualitative similar results were obtained for DD4T, DD6T and TD8T, however, with lower field effect mobilities. In some cases, leakage currents between the source and the gate electrodes could be observed, especially for DD4T and DP4T which are not uncommon for large area evaporation on the substrate [25].

III.3. Field effect mobility. Transconductance

In the saturation region, the dependence of the saturation current, $I_{D,sat}$, on the gate voltage U_G gives information about the field effect mobility μ_{FET} and the threshold voltage U_T :

$$I_{D,sat} = (C_i \mu_{FET} W/L) (U_T - U_G)^2/2. \quad (2)$$

All OFET devices were, therefore, evaluated by plotting the square root of the saturation current, $\sqrt{I_{D,sat}}$ as a function of U_G , the gate voltage.

A typical experimental *in situ* result for a DP5T transistor is shown in Fig. 5 for a drain voltage of -100 V. From the slope of the dependence of $\sqrt{I_{D,sat}}$ as a function of U_G , the square root of the field effect mobility $\sqrt{\mu_{FET}}$ can be derived. This leads to a value of $4.8 \times 10^{-3} \text{ cm}^2/\text{Vs}$ for the transistor of Fig.5.

Furthermore, the extrapolation to $I_{D,sat} = 0$ gives a value of $U_T = -48,9$ V for the threshold voltage. The dependence of $\sqrt{I_{D,sat}}$ on the gate voltage was similar as in Fig.5 for all OFETs. In this way, a comparison of field effect mobilities for the various transistors was possible, and results are given in Table 3 together with the values for the saturation currents.

The highest mobility value was found in case of DP5T. This may be correlated with its chain end molecule and possibly with the fact that it had the smoothest surface morphology.

Carrier density values, n_{FET} , may be also derived from the saturation currents if the layer thickness d_s is known:

$$n_{FET} = I_{D,sat} W / (q \mu_{FET} d_s L U_D) \quad (4)$$

where q is the elementary charge.

For a layer thickness of $d_s = 100$ nm, carrier densities were estimated in this way, and Table 4 gives values for *in situ* as well as *ex situ* measurements. As expected, the *ex situ* values are very much larger due to oxygen doping.

A usual and convenient characterization of FETs is the transconductance, defined as

$$g_m = [\delta I_D / \delta U_G]_{U_D = \text{const}} \quad (5)$$

which is related to the field effect mobility:

$$g_m = (\mu_{\text{FET}} C_i W/L) (U_G - U_T) \quad (6)$$

Typical maximum values for the transconductance are also included in Table 4, and they correlate with the mobility values of Table 3.

Transistor DP5T which has the highest field effect mobility (see. Table 3) has also the lowest carrier concentration. If the mobility is influenced by reduced carrier-carrier scattering remains an open question.

Fig. 6 shows as an example the in situ transconductance of DP 5T as a function of the gate voltage. The values for the threshold voltage U_T and for the mobility μ_{FET} deviate slightly from those obtained from the evaluation of Fig. 5.

The transconductance starts to increase at negative gate voltages which are larger than the threshold voltage. However, it does not show the typical maximum which is observed in the case of inorganic semiconductors.

IV. Conclusions

1. Most oligothiophene field effect investigations refer to end-capped chains, ECnT, and to samples exposed to air. In this paper, oligothiophenes of the type DDnT and DPnT were prepared by vacuum sublimation, and their electrical OFET properties were examined in vacuum as well as after exposure to air.
2. A basis for the evaluation are morphology changes occurring between ECnT, DDnT, and DPnT. These changes are surprisingly large, and they depend on the chain length

- and the chain-end molecule. The morphology is discussed in detail, because it must be assumed that it has an influence on the OFET performance.
3. The drain current- voltage characteristics measured in vacuum (“in situ”) have the familiar linear and saturation regions. Surprising is the influence of the interface to the gate insulator (SiO_2), suggesting that the major charge transport takes place in a thin layer near that interface.
 4. The characteristics after exposure to air (“ex situ” measurement) have essentially the same shape, however, at a drain current which is more than a factor of ten larger. This is attributed to higher p-doping due to oxygen.
 5. From the dependence of the saturation current on the gate voltage, the field effect mobility and a nominal charge density can be derived. As expected, the charge density exhibits also a strong increase due to oxygen doping after exposure to air. The highest mobility ($4.8 \times 10^{-3} \text{ cm}^2/\text{Vs}$) was observed for DP5T at the lowest charge concentration.
 6. The transconductance measured as a function of the gate voltage is correlated with the field effect mobility, as described by the conventional field effect models employed for semiconductors. However, in contrast to semiconductors, the familiar maximum of the transconductance with increasing negative gate voltage could not be observed, which still needs further clarification.

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Table 1: Sublimation temperatures

Molecule	DP4T	DD4T	DP5T	DD6T	TD8T
$T_{\text{sub}} (^{\circ}\text{C})$	150	200	200	270	380

Table 2: Particle dimensions

Oligomer	length (nm)	width (nm)	length to width ratio (r)
EC4T	564	215	2.6
EC5T	250	90	2.7
EC6T	156	27	5.7
DD4T	450	40	10
DD6T	560	6	95

Table 3: In situ saturation currents, I_{Dsat} , and field effect mobilities, μ_{FET} , for various transistors.

Molecule	DD4T	DP5T	DD6T	TD8T
$I_{\text{Dsat}} [10^{-5} \text{ mA/mm}]$	10	220	37	3.1
$\mu_{\text{FET}} [\text{cm}^2/\text{Vs}]$	3.2×10^{-5}	4.8×10^{-3}	1.0×10^{-3}	3.9×10^{-5}

Table 4: Carrier density, n_{FET} , and transconductance, g_m , for various transistors

Molecule	DD4T	DP5T	DD6T	TD8T
$g_m [10^6 \text{ mS/mm}]$	3	60	22	1
$n_{\text{FET}} (\text{in situ}) [10^{16} \text{ cm}^{-3}]$	2.93	0.54	3.85	--
$n_{\text{FET}} (\text{ex situ}) [10^{16} \text{ cm}^{-3}]$	32.5	2.6	27.5	12

Figure Captions

Fig.1. (a) End capped oligothiophenes ECnT. (b) Oligothiophenes of the type DDnT, DPnT, and TDnT (examples from top to bottom: DP4T, DD4T, DP5T, DD6T, TD8T).

Fig. 2. (a) Morphology difference between EC4T (top) and DD4T (bottom).
(b) Morphology difference between EC6T (top) and DD6T (bottom)

Fig. 3. Drain current- voltage (I_D - U_D) characteristics of a DP5T transistor for the case of *in-situ* measurements under vacuum. The top curve refers to a 10 nm thick layer measured during evaporation. The bottom curve refers to a 120 nm thick layer.

Fig. 4. *Ex situ* drain current-voltage characteristic of the same transistor as in Fig.3 after 30 min. exposure to air. Note the different current scale.

Fig. 5. *In situ* dependence of the square root of the saturation current, $I_{D,sat}$, as a function of the gate voltage for a DP5T transistor. The source drain voltage was -100 V.

Fig. 6. *In situ* transconductance dependence of a DP5T transistor as a function of the gate voltage. Source-drain voltage: -100 V.

ECnT

(a)

(b)

DP4T

DD4T

DP5T

DD6T

TD8T

Fig.1

EC4T

(a)

DD4T

Calb

EC6T

(b)

DD6T

Calb

Fig. 2

Fig 3

Fig. 4

Fig.5

Fig.6

ECnT

(a)

DP4T

DD4T

DP5T

DD6T

TD8T

(b)

Fig.1

ECnT

DP4T

DD4T

DP5T

DD6T

TD8T