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Scope and limits of organic-based thin-film transistors

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Various organic conjugated materials have been used as active semiconducting layers in thin-film transistors. The mode of operation of these devices shows that a high carrier mobility together with a low conductivity are required. Conjugated polymers and other amorphous materials exhibit a low carrier mobility, of the order of 10^{-4}–10^{-5} cm^2 V^{-1} s^{-1}, and all attempts to increase it through slight doping of the organic semioconductor have failed, owing to the existence of a direct relationship between mobility and conductivity. This behaviour can be understood from the variable range hopping mechanism which describes charge transport in these materials. On the other hand, conjugated oligomers are well-defined materials, offering various physical and chemical ways of controlling the structural organization of thin films made out of them. It is thus shown that carrier mobility is directly related to the long range structural order in these films, i.e. to the decrease of grain boundaries, leading to values close to 10^{-1} cm^2 V^{-1} s^{-1}, comparable to that of amorphous hydrogenated silicon. Besides which, conductivity in thin films of conjugated oligomers is mainly determined by the purity of the materials, allowing values lower than 10^{-7} S cm^{-1}. This independent control of mobility and conductivity allows the realization of oligomer-based thin-film transistors showing characteristics close to those of classical a-Si:H-based thin-film transistors.

1. Introduction

Organic semiconductors have raised a steadily increasing interest in the literature, particularly since conjugated materials emerged in the late 1970s. As synthesized, these materials possess a non-intentionally doped state, with a conductivity in the range of 10^{-9}–10^{-6} S cm^{-1}, and are generally *p*-type semiconducting, although ion implantation, such as Li$^+$ in polyacetylene, also allows the realization of *n*-type semiconduction. The first synthesized polyacetylene showed low stability in air and very poor processability, but new classes of environmentally stable conjugated polymers, such as polythiophenes (Tourillon & Garnier 1982) and polyphenylenevinylene (MacDiarmid *et al.* 1985) were soon proposed, the processability of which was largely improved by the use of soluble polymer precursors, or by the grafting of solubilizing alkyl or alkoxyl groups. Owing to the very low control of the polymerization reaction, these conjugated polymers are mainly amorphous, and show large distribution of conjugation lengths, together with high concentration of chemical impurities and structural defects. Later, in the mid-1980s (Fichou *et al.* 1988), a new class of better defined materials was proposed, conjugated oligomers, which raised a steadily

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increasing interest both as model compounds for their parent polymers, and also for their promising opto-electrical properties.

The characterization of these semiconductors has been carried out by the study of various devices, such as thin-film transistors, TFTs, and light emitting diodes, LEDs (Ebisawa *et al.* 1983; Tsumura *et al.* 1988; Burroughes *et al.* 1988; Assadi *et al.* 1988; Horowitz *et al.* 1989; Horowitz *et al.* 1992; Paloheimo *et al.* 1990; Akamichi *et al.* 1991; Garnier *et al.* 1993; Brown *et al.* 1994*a, b*; Servet *et al.* 1994; Dodabalapour *et al.* 1995), with a long term aim toward the development of a new area of organic electronics. Among electronic devices, TFTs in fact operate in a simple way, involving only charge injection and transport in a thin semiconductor layer. These devices are thus well adapted for analysing and discussing the basic charge transport properties of these semiconducting materials, for which two clases will be distinguished, on one hand conjugated polymers and amoprhous materials, and on the other hand conjugated oligomers.

2. Construction and mode of operation of TFTs

The first realized devices involved a highly doped silicon substrate (Tsumura *et al.* 1988; Burroughes *et al.* 1988; Assadi *et al.* 1988; Horowitz *et al.* 1989) acting as the gate electrode, on which a thermal oxide layer SiO_2 formed the insulator. Later, other materials, such as glass, were used as substrate on which a gate electrode (Ag, Al) was vacuum evaporated. The source, S, and drain, D, electrodes were then deposited on the gate oxide, using either conventional lithography techniques, or vacuum evaporation through a mask. These electrodes were made out of gold, in order to build an ohmic contact with the organic semiconductor, which was deposited in a last step, leading to a bottom gated planar device structure. Due to the low processability of most conjugated polymers, thin films were obtained through the electropolymerization of a monomer, e.g. thiophene, or through the deposition of a soluble polymer precursor. Soluble conjugated polymers, obtained by the grafting of long alkyl chains, e.g. poly(3-alkyl)thiophenes, are easily spin-casted (Assadi *et al.* 1988; Brown *et al.* 1994*b*). Another interesting route for the construction of TFT has been based on the use of Langmuir–Blodgett technique (Paloheimo *et al.* 1990). Finally, one of the most convenient and rational routes toward highly pure and defect-free semiconducting films involved vacuum deposition from a semiconductor powder in a tungsten boat, heated to the semiconductor melting point (Horowitz *et al.* 1992; Akamichi *et al.* 1991). This technique has been successfully applied to fusible molecular semiconductors, such as phthalocyanines and conjugated oligomers. The potentially interesting feature of an organic-based device originates from the fact that all its elements, substrate (polycarbonate, polyimide), insulator (polymethylmethacrylate, PMMA or polyimide), semiconductor and even electrodes (conducting ink) can be made out of organic materials, which require only low processing temperatures, opening interesting perspectives for flexible organic devices (Garnier *et al.* 1990, 1993).

These insulated-gate thin-film transistors operate as unipolar devices, in which the majority of positive charge carriers are attracted to the semiconductor–insulator interface, through negative polarization of the gate electrode, forming a conducting channel through which current flows between source and drain electrodes.

The parameters defining a TFT are the channel width, W, the channel length, L, and the capacitance per unit area of the insulator, C_i. Two main regimes are observed
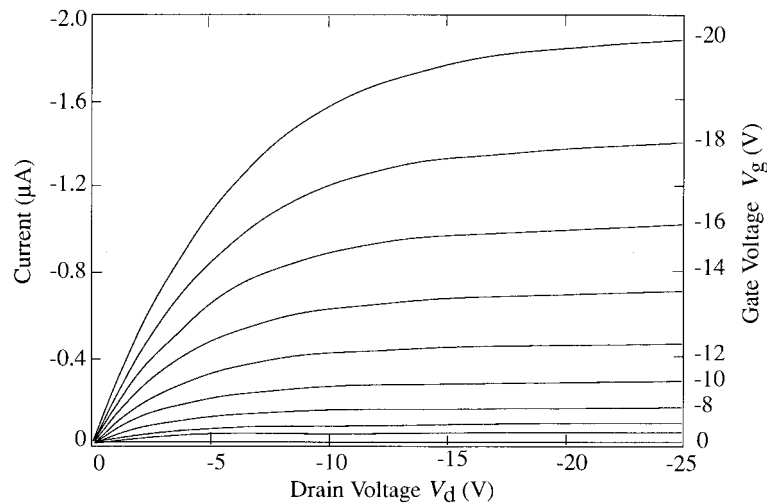
Figure 1. Experimental output $I_d = f(V_d)$ obtained with organic TFT, realized on glass substrate, with polymethylmethacrylate insulating layer ($C_i = 10$ nF), sexithiophene semiconducting layer (25 nm thick), and gold source and drain electrodes ($W = 5$ mm, $L = 50$ mm).

when plotting the drain current as a function of drain voltage, V_d, at constant gate voltage, V_g. A first linear regime, observed for low drain voltage, is followed by a saturation one, when the drain voltage exceeds the gate voltage. The variation of drain current, I_d, with applied gate voltage V_g and drain voltage V_d, is given

$$I_d = (W/L)\mu C_i[(V_g - V_T)^2 - \tfrac{1}{2}V_d^2], \tag{2.1}$$

where m is the field-effect carrier mobility, and V_T the threshold voltage. For higher values of V_d the saturation regime is described by

$$I_{d,sat.} = \tfrac{1}{2}(W/L)\mu C_i(V_g - V_T)^2. \tag{2.2}$$

Whereas the accumulation regime, equations (2.1) and (2.2), has been clearly identified, under negative gate bias for p-type organic SCs, the occurence of a depletion regime, under positive gate bias, has been seldom characterized. The thickness of this depletion layer, W_{sc}, varies according to

$$W_{sc} = (\varepsilon/C_i)[(1 + 2C_i^2(V_g - V_{fb})/(qN\varepsilon_s)^{1/2} - 1], \tag{2.3}$$

where ε_s is the dielectric constant of the semiconductor, V_{fb} is the flat band potential and N is the dopant concentration. Interestingly, the thickness of the depletion layer, W_{sc}, increases up to the total thickness of the semiconductor layer, d, which is reached at a 'pinch-off' voltage V_p, given by

$$V_p = (qNd^2/2\varepsilon_0\varepsilon_s)(1 + 2C_s/C_i), \tag{2.4}$$

where C_s is the dielectric capacitance of the semiconducting layer. Equation (2.4) is particularly interesting, as it shows that the dopant concentration, N, can be obtained by the determination of the depletion pinch-off voltage V_p.

Experimental output curves, $I_d = f(V_d)$, obtained with sexithiophene-based TFTs in the accumulation regime, figure 1, confirm the relevance of organic-based TFTs (Servet 1994).

Besides the obtained drain current, a critical characteristic of a TFT device concerns the dynamic range, or I_{on}/I_{off} ratio, which must be as high as possible, and

exceed 10^7 for practical applications:

$$I_{on}/I_{off} = 1 + C_i V_d(\mu/2\sigma d). \tag{2.5}$$

These equations allow us to define the relevance of a semiconductor for use in TFT devices. Equations (2.1) and (2.2) show that a high carrier mobility value μ is indeed needed for reaching a high current output in the 'on' position of the device, of some μA, as well as for obtaining short switching times. But equation (2.5) also shows that a high field-effect mobility is not sufficient, and that a simultaneous low value of the conductivity σ is required for reaching a high dynamic ratio I_{on}/I_{off}. In fact, when considering amorphous hydrogenated silicon, it must be remembered that its mobility reaches $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and that its conductivity is very low, $10^{-8} \text{ S cm}^{-1}$, which ensures a high dynamic I_{on}/I_{off} ratio, larger than 10^7 , for a-Si:H-based devices.

3. Conjugated materials used in organic-based TFTs

Conjugated materials can be gathered into two main classes, on one hand macro-molecular and amorphous ones, i.e. conjugated polymers, and on the other hand molecular ones, i.e. conjugated oligomers and other π-electron rich molecules. The mostly studied conjugated polymers are the following:
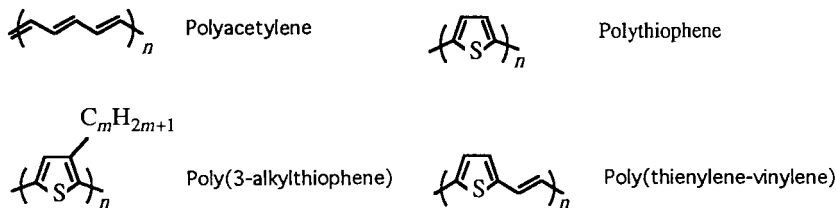
Conjugated oligomers, e.g. oligothiophenes, have been more recently used as active layers in TFTs, either unsubstituted or alkyl substituted as side or end groups (Horowitz *et al.* 1989; Akamichi *et al.* 1991; Garnier *et al.* 1993; Waragai *et al.* 1993). Unsubstituted oligothiophenes, from terthiophene 3T to octithiophene 8T, and α,ω-dialkyl substituted oligothiophenes, from dialkylterthiophene to dialkyloc-tithiophene, have been deposited by vacuum evaporation:
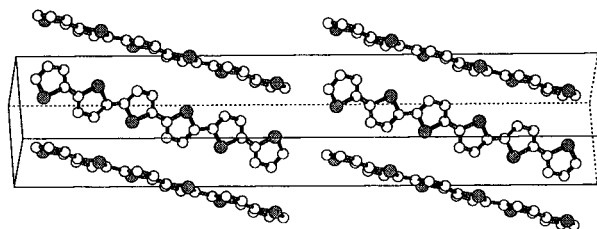
Other classes of π electron rich molecules have been studied in the last ten years, such as pentacene (Horowitz *et al.* 1992), scandium, lutecium and thullium diphthalo-cyanines, nickel and zinc phthalocyanines (Guillaud *et al.* 1990), fullerene (Hoshi-mono *et al.* 1993), and tetracyanoquinodimethane TCNQ (Brown *et al.* 1994*a*), which were deposited by vacuum evaporation.

These organic semiconductors present distinct charateristics from inorganic cova-lent semiconductors. Inorganic semiconductors, e.g. silicon, present a three dimen-sional architecture, in which atoms are held together by strong covalent bonds, with

energies of the order of 76 kcal mole^{-1} in the case of Si–Si bonds. Semiconductivity appears then as a collective property, which develops with the constitution of the three-dimensional architecture of the material. Owing to the strong interatomic bonds, the width of the conduction and valence bands is large, one may expect significant carrier mobility values. These materials are highly sensitive to chemical impurities and to surface states, owing to the presence of dangling bonds at their surface. On the other hand, organic molecular semiconductors are made out of molecules, which are only held together by weak van der Waal forces, of some 10 kcal mole^{-1}. The electronic properties of the solid are already present in the individual molecules, as shown for instance by the closeness of the absorption spectra of individual molecules and of their assembly in the solid state. These features indicate that charge transport in molecular solids operates mainly through individual states. Furthermore, the width of the valence and conduction bands is small, which suggests that carrier mobility should be much lower in these solids. Finally, these organic molecular materials are less sensitive to chemical impurities, undergoing much fewer substitutions, and the quasi-absence of dangling bonds prevents them from high sensitivity to surface states. These considerations show that organic molecular materials cannot be expected to present as high mobilities as those of their inorganic counterparts, which reach some 10^3 cm^2 V^{-1} s^{-1} for monocrystalline silicon. On the other hand, it has been shown that carrier mobility in monocrystalline condensed aromatic hydrocarbons reaches values in the range of 1–10 cm^2 V^{-1} s^{-1}, at room temperature. Thus, owing to the ease of realizing highly structured films of organic molecular compounds, one can reasonably hope that organic semiconducting films will be able to reach mobility values in the range of 10^{-1}–1 cm^2 V^{-1} s^{-1}, close to those shown by a-Si:H, opening a potentially interesting field of organic-based devices.

4. Device characteristics

Electrical characteristics obtained in the literature will be discussed in terms of the two classes of conjugated materials defined previously.

(a) *Conjugated polymers and amorphous materials*

The main data obtained with conjugated polymers and other amorphous materials are gathered in table 1. These semiconductors generally behave as *p*-type, unless quoted.

The range of values, given for some compounds, indicates that various experimental attempts have been carried out for increasing the electrical properties, the lowest values of conductivity and mobility relating to as-prepared films. The data indicate that as-prepared organic semiconducting films possess very low mobilities, in the range of 10^{-8}–10^{-4} cm^2 V^{-1} s^{-1}, which have been interpreted in terms of poor efficiency of charge hopping in highly disordered materials, originating from self-localization and defects. In order to improve the field-effect mobility of these organic SCs, their doping level has been intentionnally increased, either electrochemically, in the case of electropolymerized polythiophene (Tsumura *et al.* 1988), or chemically, in the case of poly(3-alkylthiophene) (Assadi *et al.* 1988) poly(DOT)3 (Brown *et al.* 1994*b*), C60 (Hoshimono *et al.* 1993) and TCNQ (Brown *et al.* 1994*a*). Some other attempts have been based on the 'annealing' of the semiconducting film, often realized under oxygen atmosphere (Guillaud *et al.* 1990). Results, table 1, confirm that

Table 1. *Electrical characteristics of conjugated polymers and amorphous materials*

material	deposition technique	conductivity (S cm^{-1})	mobility (cm^2 V^{-1} s^{-1})	reference
polyacetylene	polymer	10^{-5}	10^{-5}	Ebisawa *et al.* (1983)
polyacetylene	precursor	10^{-5}	10^{-4}	Burroughes *et al.* (1988)
polythiophene	electropoly	10^{-6}–10^{-5}	10^{-6}–10^{-5}	Tsumura *et al.* (1988)
polyalkylthiophene	spin coating	10^{-8}–10^{-5}	10^{-8}–10^{-5}	Assadi *et al.* (1988)
poly(DOT)$_3$	spin coating	10^{-8}–10^{-5}	10^{-6}–10^{-3}	Brown *et al.* (1994*b*)
polythienylenevinylene	precursor	10^{-6}–10^{-4}	10^{-5}–10^{-3}	Fuchigami *et al.* (1993)
Lu, Tm diphthalocyanine	vac. evap.	10^{-4}–10^{-3}	10^{-4}–10^{-2}	Guillaud *et al.* (1990)
fullerene (*n*-type)	vac. evap.	10^{-8}–10^{-5}	10^{-5}–10^{-2}	Hoshimono *et al.* (1993)
TCNQ (*n*-type)	vac. evap.	10^{-10}–10^{-6}	10^{-10}–10^{-4}	Brown *et al.* (1994*a*)

a significant increase of field-effect mobility has been obtained by such doping, by almost two order of magnitude, evidencing a relationship between intentional doping and carrier mobility (Tsumura *et al.* 1988; Assadi *et al.* 1988; Brown *et al.* 1994*b*, Guillaud *et al.* 1990). On the other hand, conductivity, which is given by the relation $\sigma = N_\mathrm{f} q\mu$, where N_f is the density of free carriers, is also well known to increase with the doping level, according to a $\sigma \sim N^\gamma$ relationship. It follows that a direct relationship between mobility and conductivity, $\mu \sim \sigma^{\gamma/\gamma-1}$, can be expected, which has been indeed experimentally observed (Brown *et al.* 1994*a*, *b*). Such behaviour can be easily interpreted by considering the mechanism of charge transport. As a matter of fact, the hopping mechanism associated with amorphous organic semiconductors infers a strong dependence of charge transport to the hopping distance, R, in the form of $\sigma = 2q^2 R^2 \nu_\mathrm{ph} N(E_\mathrm{F}) \exp(-2\alpha R)(-W/kT)$, where R is the hopping distance, $N(E_\mathrm{F})$ is the density of states at the Fermi level, α is the electronic wavefunction overlap and W is the energy difference between initial and final electronic states. The increase of doping level leads to the increase of $N(E_\mathrm{F})$, and to the decrease of the hopping distance R, which results thus in the increase of conductivity and also of carrier mobilty.

Thus increase of the doping level, N, led to a significant increase of mobility, up to $\mu = 10^{-3}$ cm^2 V^{-1} s^{-1}, but also led to a simultaneous increase of the conductivity, up to values of the order of 10^{-3} S cm^{-1}. Large ohmic currents are therefore expected, which increase I_off currents and dramatically reduce the dynamic ratio of the corresponding devices. The simultaneous increase of mobility and conductivity thus invalidates this approach for the improvement of charge transport efficiency in conjugated polymers and disordered materials.

(*b*) *Conjugated oligomers*

On the other hand, early work on conjugated oligomers revealed a significant increase in field-effect mobility, whereas conductivity remained low, suggesting another transport mechanism. These first results stimulated a large amount of interest, all the more since conjugated oligomers offer the unique advantage of high purity, well-defined structure and monodisperse conjugation length, opening the way for the rationalization of structure effects on electrical properties of conjugated materials (Garnier *et al.* 1993; Servet *et al.* 1994).

The first results on sexithiophene, 6T, showed a large increase of mobility, up to some $2 \times 10^{-3}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$, accompanied with a relatively low conductivity, $10^{-6}\,\mathrm{S\,cm^{-1}}$. Structural characterizations by X-ray diffraction, XRD, evidenced that thin films of 6T were highly ordered, made of stacks of planar 6T molecules, which suggested a transport mechanism analogous to the one occuring in charge transfer complexes, e.g. TTF–TCNQ. These complexes are also made of regular stacks of donor and acceptor molecules, with short intermolecular distances, allowing important overlap of the π-orbitals of neighbouring molecules. The charge propagates preferentially along the stacking axis of donor (or acceptor) molecules, through the overlapping π-orbitals, and it has been largely shown that structural organization of molecules in the solid plays a major role. Following this model, charge transport efficiency in conjugated oligothiophenes would require the molecules to remain fully planar and parallel to each other, in the closest possible packing, with the longest possible range order, for avoiding grain boundaries known to be very efficient traps for charges.

Various routes have been followed for an *a priori* control of the structural organization of molecules in the semiconducting film, considered as a molecular assembly. Among them, physical approaches involve either the modification of the experimental conditions used for film deposition, or a film treatment. Another route uses a chemical approach, through the engineering of the semiconductor molecules, in order to induce self-assembly properties. Finally, an ultimate step concerns the growth of a single crystal of the organic semiconductor, the properties of which can be considered as the achievable limits for charge transport.

(i) *Temperature of substrate during film deposition*

The structural organization of organic materials deposited as thin films on a substrate can be controlled by the temperature of the substrate, as well as by the rate of evaporation. A detailed study has been carried out on sexithiophene, 6T, which was deposited as 2–3 µm thick films on Si substrates, and analsed by XRD in θ–2θ scanning symmetrical reflection mode, by polarized UV-visible spectroscopy and also by scanning electron microscopy.

Experimental results evidenced the polymorphism of 6T. When the substrate is held at 77 K, molecular motions are frozen, and the first deposited 6T molecules nucleate and crystallize preferentially with their long axis lying parallel to the substrate plane. At room temperature and low deposition rate, 6T molecules adopt another crystallite orientation, with their c-axis perpendicular to the substrate plane. At room temperature and high deposition rate, some 6T molecules remain also frozen on the substrate, and the 6T film involves the two preceeding populations, with crystallites having their c long axis either parallel or perpendicular to the substrate plane, corresponding respectively to the kinetically or thermodynamically favoured orientation of the crystallites. When deposited at 190 °C, films of 6T exclusively show several orders of meridional 00l reflections, which means that a great majority of crystallites are grown with their c-axis perpendicular to the substrate plane. When further heating the substrate to 260 °C, the XRD spectrum only reveals low angle 00l reflections, indicating that the 6T films are entirely crystallized, with the crystallite (a, b)-face parallel, and c-axis perpendicular to the substrate plane, respectively. Polarized UV-visible spectroscopy, carried out on these films deposited at various substrate temperatures (Servet *et al.* 1994), confirmed these preferential organization of 6T molecules. Finally, the morphology of these films has been analysed by the

use of scanning electron microscopy (Servet *et al.* 1994). When deposited at room temperature, isotropically distributed crystallites are observed, of some 50 nm diameter. When the substrate is held at 190 °C, the crystallites show an elongated shape, with larger dimensions reaching $30 \times 200 \, \text{nm}^2$, and close packing arrangement. On the last sample realized at 260 °C, the 6T layer shows discontinuous surface, arising from a possible cellular growth. Long lamellae, 50 nm wide, are observed, most of them being interconnected, giving rise to a network over the film surface. These results confirm that the control of substrate temperature allows us to monitor the grain size and shape, together with the homogeneity of structural organization, providing highly organized molecular layers, with low concentration of grain boundaries.

More recently, another way has been described for improving the structural organization, which involves the micromelting of a film of conjugated material. As-sublimed polycrystalline films of 6T, with isotropic grain size of about 50 nm, have been submitted to short pulse heating, which resulted in a significant increase of the crystallite size, up to some microns (Dodabalapur *et al.* 1995). In conclusion, these structural characterizations confirm that the control of susbtrate temperature and evaporation rate for film deposition, together with the annealing of the film, allows control of the structural organization of oligothiophene molecules in their solid state.

(ii) *Chemical engineering of molecules*

Chemical engineering of these oligothiophenes represents an interesting alternative route for controlling the molecular organization in the film at a mesoscopic level. Oligothiophene molecules have been substituted, at their α, ω-end positions, with alkyl chains, which are known to present intermolecular self-recognition properties (Garnier *et al.* 1993; Waragai *et al.* 1993). Detailed spectroscopic studies under polarized light, together with XRD spectra, have confirmed that, even when deposited on substrate at room temperature, films of dihexylsexithiophene, DH6T, are highly structured. Numerous high-order 00l reflections are observed in the XRD spectrum, up to the 34th order, in agreement with results obtained on dimethylquaterthiophene, indicating that the crystallites have their long c-axis perpendicular to the substrate plane. Furthermore, structural organization at the mesoscopic level, obtained from X-ray pole figures, confirmed the existence of almost one single population of molecules, standing up on the substrate plane, with their (a, b)-face as contact plane. The almost complete structuration of molecular layers, realized on a substrate at room temperature, must be associated with the stacking properties brought by the terminal alkyl groups, which are already known for inducing long range ordering and mesophases. These films can be described by a *liquid-crystal-like superstructure*, imposed by the terminal alkyl groups for the whole molecular assembly, as represented in figure 2. Alkyl–alkyl recognition, based on lipophilic–hydrophobic interactions, brings a strong driving force for a close packing of the conjugated sexithiophene backbones, and also, most importantly, for a long range molecular ordering.

These 6T films, with various structural organization, have been characterized concerning their electrical properties, i.e. parallel and perpendicular electrical conductivity, together with field-effect mobility, table 2. The conductivity parallel to the susbtrate surface, $\sigma_{\parallel}$, has been measured using a four-probe technique, and the perpendicular conductivity, $\sigma_{\perp}$, from a sandwich type structure, with two gold contacts, Au–6T–Au. Parallel conductivity decreases when increasing the temperature, this can be ascribed to the desorption of impurities on a heated substrate. On the other hand, the very large conductivity shown by a 6T film deposited on a substrate
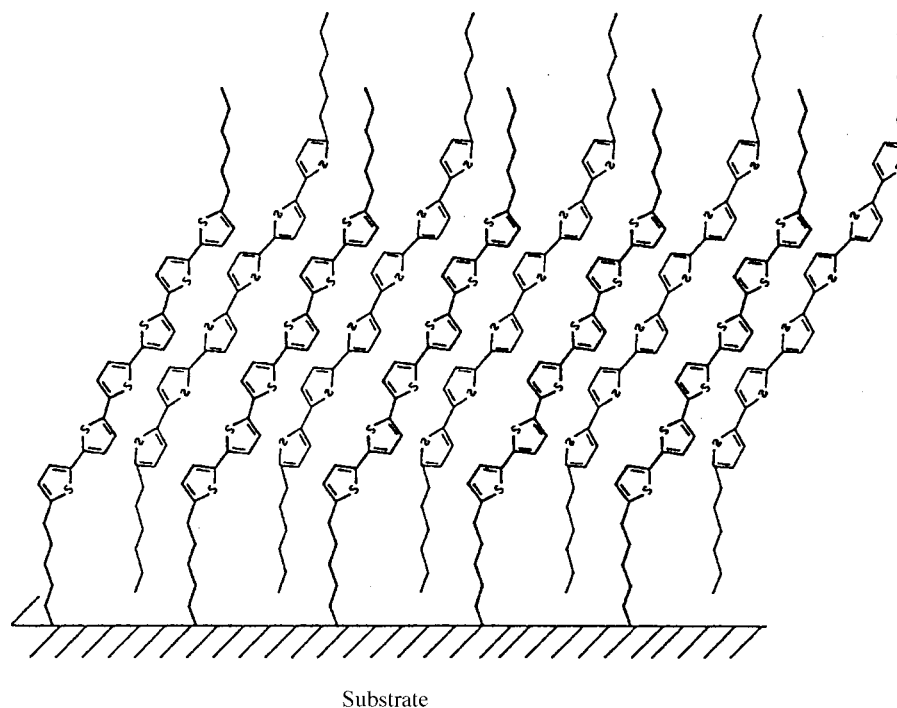
Substrate

Figure 2. Schematic representation of an α, ω-dihexylsexithiophene monolayer on substrate.

maintained at 77 K can be attributed to the pollution of the film during vacuum deposition on a cold substrate. The perpendicular conductivity also decreases when increasing the substrate temperature, which shows that the conditions used for film deposition allow a further purification of the molecular material, which should significantly improve its electrical properties. Importantly, the anisotropy of conductivity increases with substrate temperature, in agreement with the proposed scheme of charge transport process occuring along the stacking axis of the 6T molecules, i.e. parallel to the substrate plane. The increase of anistropy of conductivity $\sigma_\parallel/\sigma_\perp$ follows the increase in molecular ordering perpendicular to the substrate surface, as previously shown from structural characterizations.

The field-effect mobility, μ, measured on TFTs realized on glass substrate, was calculated in the linear regime of I_d–V_d curves, from equation (2.1). The lowest value is obtained for a film deposited at room temperature, which has been shown to be the less organized one, with two orientations of crystallites. When 6T films are deposited on a heated substrate, the observed field-effect mobility increases rapidly, up to one order of magnitude, reaching 2.5×10^{-2} cm^2 V^{-1} s^{-1}. This value, recently confirmed on TFT devices with micronic sized channel (Dodabalapur *et al.* 1995), brings a clear confirmation of the predominant role played by structural organization of the semiconducting film, and also on the control which can be exerted by the experimental conditions used for the film deposition.

As compared to unsubstituted oligothiophenes, α, ω-dialkyloligothiophenes, e.g. α, ω-dihexylsexithiophene DH6T, present an increased parallel conductivity, $\sigma_\parallel$, together with a larger anisotropy ratio, which reflects the longer range order and fewer defects existing in layers of these conjugated materials. More significantly, the field-effect mobility increases very largely, reaching $\mu = 8 \times 10^{-2}$ cm^2 V^{-1} s^{-1}. This value,

Table 2. *Electrical characteristics of sexithiophene, 6T, and α,ω-dihexylsexithiophene, DH6T, films deposited on substrates at various temperatures*

(From Garnier *et al.* (1993) and Servet *et al.* (1994).)

substrate temperature	morphology	molecular orientation	conductivity (S cm^{-1})		mobility (cm^2 V^{-1} s^{-1})
			$\sigma_\parallel$	$\sigma_\perp$	μ
6T, RT	isotropic grains diam. 50 nm	paral. & perpend. /substrate	2×10^{-7}	1.5×10^{-6}	2×10^{-3}
6T, 190 °C	long grains 30×200 nm^2	perpend. /substrate	—	9×10^{-7}	9×10^{-3}
6T, 260 °C	connected long grains 50×400 nm^2	perpend. /substrate	4×10^{-9}	1.2×10^{-7}	2.5×10^{-2}
DH6T, RT	liquid crystal	perpend. /substrate	5×10^{-7}	6×10^{-5}	8×10^{-2}

close to that of a-Si:H gives reasonable hope for real applications of these materials as active layers in thin-film transistors. The most important conclusion concerns the potential interest of the chemical approach for controlling the structural organization of oligothiophene films, considered as molecular assemblies. Chemical engineering of oligothiophene molecules, realized by end-substitution with alkyl groups, is an elegant and powerful way for inducing self-assembly properties to the oligothiophene molecules, leading to liquid-crystal-like structured layers.

(iii) *Single crystal*

Single crystals represent the ultimate molecular organization, and should allow us to set the limit of achievable electrical properties. Our group succeeded recently in growing single crystals of unsubstituted sexithiophene, whose size and shape are compatible for the fabrication of field-effect transistors. A complete crystallographic study has been carried out on 6T single crystals (Horowitz *et al.* 1995), which showed that the unit cell is monoclinic and contains four molecules closely packed in a herringbone structure, as shown in figure 3.

6T single crystals appear as small plates, with dimensions of some 3×3 mm^2 surface and 5–10 μm thickness. The long axis of the monoclinic unit cell is perpendicular to the crsytal plane, which means that the stacking axis of the 6T molecules runs parallel to the large surface of the crystal. The most significant feature of the crystal structure concerns the complete planarity of the molecules, which is even more planar than that observed in terthiophene single crystals. Furthermore, 6T molecules lie strictly parallel to one another, ensuring a very large overlap of their π molecular orbitals. Electrical characterizations of 6T single crystals have shown that the conductivity is very low, with an upper limit of 10^{-9} S cm^{-1}, which must be related to a very low doping level. Field-effect transistors have also been fabricated from 6T single crystals (Horowitz *et al.* 1995a). Due to experimental difficulties for realizing a field-
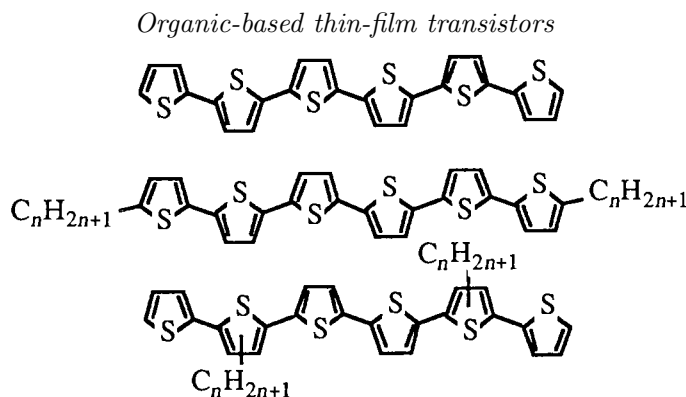
Figure 3. Crystal structure of sexithiophene.

effect transistor on such crystal, the obtained value, $\mu = 7 \times 10^{-1}$ cm^2 V^{-1} s^{-1} can be considered as a rough value for field-effect mobility in a single crystal of 6T.

Interestingly, the amplification characteristics of a 6T single-crystal-based transistor can be used for the calculation of the dopant concentration using equation (2.4). The observed pinch-off voltage, of $+30$ V, corresponds to the completely depleted semiconductor, when depletion width W_{sc} reaches the thickness of the semiconducting crystal. The dopant concentration calculated from equation (2.4), $N = 3 \times 10^{14}$ cm^{-3}, corresponding to 0.2 ppm intentionally doped conjugated materials, of about 10^{17}–10^{18} cm^{-3}. This very low concentration indicates the high purity of the crystallized material.

5. Charge transport in conjugated oligomers

Even if practical applications of organic-based devices in electronics are potentially attractive, one of the most interesting goals of the electrical characterizations of conjugated polymers and oligomers concerns the analysis of the charge transport mechanism in these materials. With this aim, studies have been performed on temperature effects on conductivity and on field-effect mobility (Paloheimo *et al.* 1990; Waragai *et al.* 1993; Horowitz *et al.* 1995*b*). Analysis carried out on thin films of fullerene, C$_6$0, has already revealed that field-effect mobility is thermally activated at fixed gate voltage, and that the activation energy decreases with increasing gate voltage, this has been attributed to an exponential distribution of traps in the gap, as reported for amorphous hydrogenated silicon. More recently, such analysis has been performed on 6T and on α, ω-dihexylsexithiophene, DH6T, from 100–300 K (Horowitz *et al.* 1995*b*), which revealed two temperature-dependent regimes. At temperatures above 150 K, the conductivity is thermally activated, with an activation energy of 0.22 eV for DH6T and of 0.26 eV for 6T. At lower temperature, a change of the slope is observed in the Arrhenius plot of conductivity. The field-effect mobility also shows a strong gate-bias-dependent activation energy and it tends to saturate at both high gate bias and high temperature. These data were analysed within the frame of a multiple trapping and release model, and shown to fit with a double exponential distribution, associated to the presence of deep and tail states near the transport level, which can be compared to the case of a-Si:H. Importantly, the microscopic mobility μ_0 of both 6T and DH6T are found to be comparable, the lower effective mobility observed in the case of 6T being attributed to the higher density of deep traps. Following the results obtained in the structural analysis of

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conjugated oligomers, these traps can be associated to grain boundaries, which have been shown in higher concentration for 6T films. When temperature decreases the probability of thermal release from localized traps diminishes, and a transition from trapping to thermally activated hopping has been proposed as the dominant transport mechanism, in agreement with the significant change of slope of the Arrhenius plot. Furthermore, a back transition from hopping to trapping can be observed at low temperature, when increasing the gate voltage. Under increasing gate bias, traps become filled with injected charges, and, all deep traps being filled, charge transport switches back to a multiple trapping and release mechanism, in agreement with the fast increase of saturation current with gate voltage. Eventually, all traps can become filled, which means that any additional charge will then move freely with the microscopic mobility.

The proposed multiple trapping and release mechanism appears to bring a satisfying picture of the charge transport process in conjugated oligomers, pointing out the determining role played by traps (grain boundaries, chemical impurities). This model accounts for the large increase in field-effect mobility observed when depositing 6T on a heated substrate, which results in the increase of the crystallite size, and also when using liquid-crystal-like structured DH6T. Thus, in the case of conjugated oligomers, the proposed trapping mechanism allows us to understand how field-effect mobility of thin films can be increased almost to its upper limit, corresponding to a single crystal. It also allows us to understand that large I_{on}/I_{off} ratio for the drain current can be achieved, through the decrease of dopant concentration.

6. Conclusion

Thin film transistors have been fabricated from various organic semiconductors, including conjugated polymers and oligomers. Two categories of behaviour can be differentiated. First, in most of the conjugated polymers and in a large number of 'amorphous' molecular materials, conduction is governed by a hopping mechanism. Structural disorder, grain boundaries together with large density of chemical impurities impose a very low efficiency for charge transport, with carrier mobilities μ of about 10^{-5} cm^2 V^{-1} s^{-1}. In agreement with the hopping mechanism, field-effect mobility depends on the doping level N, which can be experimentally increased. However, conductivity also increases simultaneously, and TFTs made with these materials present an inherently very poor I_{on}/I_{off} dynamic ratio. The second category corresponds to molecular materials, such as short conjugated oligomers. In these materials, charge transport obeys a multiple thermal trapping mechanism, and is hence only dependent on the density of traps, whereas conductivity depends on the doping level. Highly ordered and very pure materials allow us to reach both a high mobility, of the order of 10^{-1} cm^2 V^{-1} s^{-1}, and also a low conductivity, of the order of 10^{-7} S cm^{-1}, which meet the requirements for efficient TFT devices. Highly crystallized films can be realized by adjusting the experimental conditions for film deposition. Long range molecular ordering in the semiconducting film can also be easily achieved by an elegant chemical route, involving the substitution, at both ends of the conjugated molecule, of alkyl groups, which bring self-assembly properties to these molecules.

References

Akamichi, H., Waragai, K., Hotta, S., Kano, H. & Sakati, H. 1991 *Appl. Phys. Lett.* **58**, 1500–1502.

Assadi, A., Svensson, C., Wilander, M. & Inganäs, O. 1988 *Appl. Phys. Lett.* **53**, 195–197.

Burroughes, J. H., Jones, C. A. & Friend, R. H. 1988 *Nature* **335**, 137.

Brown, A. R., Deleeuw, D. M., Lous, E. J. & Havinga, E. E. 1994*a Synth. Met.* **66**, 257–261.

Brown, A. R., Deleeuw, D. M., Havinga, E. E. & Pomp, A. 1994*b Synth. Met.* **68**, 65–70.

Dodabalapur, A., Torsi, L. & Katz, H. E. 1995 *Science* **68**, 270–271.

Ebisawa, F. , Kurosawa, T. & Nara, S. 1983 *J. Appl. Phys.* **54**, 3255–3259.

Fichou, D., Horowitz, G., Nishikitani, Y. & Garnier, F. 1988 *Chemtronics* **3**, 176–178.

Fuchigami, H., Tsumura, A. & Koezuka, H. 1993 *Appl. Phys. Lett.* **63**, 1372–1374.

Garnier, F., Horowitz, G., Peng, X. Z. & Fichou, D. 1990 *Adv. Mater.* **2**, 592–594.

Garnier, F., Yassar, Y., Hajlaoui, R., Horowitz, G., Deloffre, F., Servet, B., Ries, S. & Alnot, P. 1993 *J. Amer. Chem. Soc.* **115**, 8716–8721.

Garnier, F., Hajlaoui, R., Yassar, A. & Srivastava, P. 1994 *Science* **265**, 1684–1686.

Guillaud, G., Al Sadoun, M., Maitrot, M., Simon, J. & Bouvet, M. 1990 *Chem. Phys. Lett.* **167**, 503–506.

Horowitz, G., Fichou, D., Peng, X. Z., Xu, Z. & Garnier, F. 1989 *Solid. State Comm.* **72**, 381–784.

Horowitz, G., Peng, X. Z., Fichou, D. & Garnier, F. 1992 *Synth. Met.* **51**, 419–424.

Horowitz, G. Bachet, B., Yassar, A., Lang, P., Deloffre, F., Fave, J. L. & Garnier, F. 1995*a Chem. Mater.* **7**, 1337–1342.

Horowitz, G., Hajlaoui, R. & Delannoy, P. 1995*b J. Physique* III **5**, 355–371.

Hoshimono, K., Fujimori, S. & Fujita, S. 1993 *Jap. J. Appl. Phys.* **32**, L1070–L1073.

MacDiarmid, A. G., Chiang, J. C., Mu, S. L., Somasini, N. L. D. & Wu, W. 1985 *Mol. Cryst. Liq. Cryst.* **121**, 187–193.

Paloheimo, J., Kuivaleinen, P., Stubb, H., Vuorimaa, E. & Yli-Lahti, P. 1990 *Appl. Phys. Lett.* **56**, 1157–1159.

Servet, B., Horowitz, G., Ries, S., Lagorse, O., Alnot, P., Yassar, A., Deloffre, F., Srivastava, P., Hajlaoui, R., Lang, P. & Garnier, F. 1994 *Chem. Mater.* **6**, 1809–1815.

Sze, S. M. 1981 *Physics of semiconductor devices.* New York: Wiley.

Tourillon, G. & Garnier, F. 1982 *J. Electroanalyt. Chem.* **135**, 173–178.

Tsumura, A., Koezuka, H. & Ando, Y. 1988 *Synth. Met.* **25**, 11–23.

Waragai, K., Akimichi, H., Hotta, S., Kano, H. & Sakaki, H. 1993 *Synth. Met.* **55–57**, 4053–4058.

Discussion

H. J. GEISE (*University of Antwerp, Belgium*). The single crystals of the oligo-thiophenes you obtained are long but very thin and hence probably suffer from large mosaic spread. Does Dr Garnier know this spread and does this spread become intolerable?

F. GARNIER. In such thin crystals, mosaic-type structures can be found, they can be observed using a microscope and polarized light. But in the present case, of sexithiophene single crystals, we noticed that a significant amount of the synthesized crystals were optically pure and mosaic free. These crystals were selected and used for the characterizations described here.