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Polymorphism and Charge Transport in Vacuum-Evaporated Sexithiophene Films

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The influence of deposition temperature on structure, orientation, and morphology of vacuum-evaporated sexithiophene films has been studied by using X-ray diffraction, UV-visible spectroscopy and scanning electron microscopy. We correlate this with the mobility of these films as measured in field-effect transistors. The X-ray study based on meridional 00 l reflections shows evidence for various crystalline phases depending on the substrate temperature during vapor deposition. A high degree of orientation can be achieved even in several-micrometer-thick films deposited above 190 °C. It is shown that the field-effect mobility is substantially enhanced for deposition temperatures close to the melting point (290 °C), which is associated with a suitable orientation (002 being the single contact plane) and eventually a favorable crystalline structure and coalescent lamellae morphology.

Introduction

Nonintentionally doped conjugated polymers have known a renewed interest since it was shown that these organic compounds can be used as active materials in field-effect transistors¹ and light-emitting diodes.² Previous works from the laboratory of CNRS-Thiais³ and elsewhere^{4,5} have demonstrated that the electrical transport in conjugated macromolecules is substantially enhanced in well-defined oligomers. From correlated X-ray diffraction (XRD) and electrical measurements, we have shown that this enhancement is associated with the better orientation of the molecules in thin solids films.⁶ Evidence for a strong correlation between orientation and electrical transport properties has been further given by the comparison between films of unsubstituted linear oligothiophenes and oligothiophenes substituted by linear alkyl groups at terminal positions^{4,7} (α,ω -DH6T). The self-organizing trend brought by the alkyl group results in a preferential orientation of the substituted oligomers with their long molecular axes roughly perpendicular to the substrate plane, and a subsequent increase by 2 orders of magnitude of the

field-effect mobility with respect to that of the unsubstituted molecule. For the case of unsubstituted sexithiophene (6T) vapor deposited at room temperature, we have observed the coexistence of molecules oriented with their long axes either parallel or perpendicular to the substrate plane.⁶

During the course of our work, Bäuerle and co-workers have reported a study of vapor-deposited ultrathin solid films of oligothiophene.⁸ From UV-visible, IR, and fluorescence-polarized light spectroscopy measurements, they showed that films of unsubstituted oligothiophenes in the monolayer range are strongly oriented with the long molecular axes perpendicular to the plane of the substrate but that this orientation is lost on thicker films. However, it has been reported by Yamamoto and co-workers⁹ that the crystallinity and orientation of vacuum-evaporated polythiophene were substantially improved by raising the substrate temperature from 20 to 150 °C.

In the present paper, we show that vapor deposition on a heated substrate up to nearly 300 °C considerably improves the orientation of thick sexithiophene films. Evidence for this orientation is given by XRD and polarized UV-visible spectroscopy. In addition, we found that the crystal structure as well as the morphology observed by scanning electron microscopy also lead to a beneficial effect on electric charge transport.

Experimental Section

The synthesis of 6T and of its dihexyl end-substituted derivative α,ω -DH6T have been given previously.⁷

Sexithiophene films (2–3 μm thick) were vacuum evaporated on Si substrates held at controlled temperatures and characterized by X-ray diffraction. The XRD analyses were carried out by using the Bragg–Brentano method (θ – 2θ scanning) in symmetrical reflection mode, with Cu K α radiation and a graphite monochromator. The XRD spectra evi-

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dence the X-ray intensities diffracted by the hkl Bragg planes parallel to the substrate. Occasionally, we have used a four-circle diffractometer (Seifert equipment as described in ref 6) in order to explore another direction by tilting the sample of a given χ angle.

The morphologies of 100-nm-thick 6T films have been observed by using a scanning electron microscopy (Model 150F of Topcon) equipped with a field-effect electron gun which can be used at low voltage for organic compound imaging, in order to limit the damage due to irradiation. In fact, two configurations have been used for SEM observations: (i) with AuPd metallization and a voltage of 30 kV; (ii) as-deposited with a voltage of 5 kV. Both configurations gave similar results, which eliminates any artifact due to metallization. The micrographs of metallized 6T films are presented in this report since a better resolution (about 20 Å) is achieved with a voltage of 30 kV. UV-visible spectroscopy was performed on films deposited on quartz substrates, with a Varian Cary 2415 spectrophotometer. All spectra, including those recorded under polarized light, were corrected for the absorption of the substrate.

The fabrication and characterization of field-effect transistors have been extensively described previously.³ The devices consist of a thermally oxidized highly doped silicon wafer, on top of which a 6T film, about 100 nm thick, is vacuum evaporated. The silicon substrate acts on the gate electrode. Source and drain electrodes are deposited by evaporating two gold stripes on top of the 6T film. The current-voltage characteristics of the transistor were recorded with a Hewlett-Packard 4140 B picoammeter/dc voltage source.

Results

X-ray Diffraction. In the present work, we must point out that vacuum evaporation is performed with a low deposition rate ranging from 1 to 5 Å/s. The 6T thin films deposited at various substrate temperatures were characterized by XRD θ - 2θ scanning in symmetrical reflection mode.

The XRD spectrum of 6T slowly deposited at room temperature (Figure 1a) is obviously different from that of a 6T film obtained by a rapid evaporation⁶ (Figure 1b). In particular, we can observe an appreciable shift of the small-angle diffraction peak indicating a variation of the long interlayer spacing between these two films (about 23.7 Å for the slow deposition and 24.4 Å for the fast deposition). This demonstrates the existence at room temperature of two crystalline forms in unsubstituted 6T, one corresponding to the most stable form (α phase). The second one is metastable (β phase) and kinetically favored, i.e., produced by a rapid crystallization. The XRD spectrum of 6T deposited at 77 K (Figure 1c) is similar to that of the 6T film fastly deposited at room temperature (Figure 1b), except that no low-angle diffraction is observed. This indicates that preferential orientation consists of molecules lying parallel to the substrate plane. Since the molecular motions are frozen on a substrate cooled at the temperature of liquid nitrogen, the first adsorbed 6T molecules would nucleate and crystallize preferentially with this orientation, in agreement with our previous expectations.⁶ At low-angle peak could be observed by tilting the sample by $\chi = 70^\circ$ on the four-circle diffractometer. The resulting d spacing (interlayer spacing) of 24.4 Å indicates a crystal structure similar to that of the β phase, previously reported for a film deposited at room temperature with a high deposition rate.⁶

The XRD spectrum of the 6T film deposited at 190 °C shows exclusively several orders of meridional 00/

reflections (Figure 1d). This means that a great majority of the crystals are grown with their (a,b) face (monolayer plane) parallel to the substrate. In contrast to the last case, the molecules adsorbed can stand up and crystallize in a self-organized way with a single preferential 002 orientation. Here, the lower interlayer spacing of 22.42 Å indicates a different structure which can be designated as γ phase. A similar long spacing has been recently reported in the cases of sublimated 6T powder and film crystallized from solution.¹⁰ This phase still exists in a film deposited at 220 °C, but the XRD spectrum evidences also the appearance of another set of small meridional peaks in the low-angle side. The intensities of these new peaks are found to increase as the substrate temperature is raised near the melting point (about 290 °C). We have selected a temperature of 260 °C for the X-ray study in order to limit the desorption of the molecules. At this temperature, the XRD spectrum reveals only the last series of low-angle 00/ reflections (Figure 1e) which is associated to a new crystalline phase (δ phase). Here again, the 6T film is completely crystallized with (a,b) face parallel to the substrate. Surprisingly, the long d spacing of 36.3 Å does not correspond to the monolayer thickness in 6T) but rather is 1.5 times the expected value.

The experimental facts clearly evidence the polymorphism of 6T depending on the conditions of film deposition. The existence of various crystalline forms can be explained by several possible molecular packings commonly based on the herringbone structure. In our previous work,⁶ we have already explored two monoclinic arrangements with lattice constants given by (i) $a \sin \beta = 5.56$ Å, $b = 7.80$ Å (unique axis), $c \sin \beta = 46.5$ Å, and (ii) $a \sin \beta = 7.80$ Å, $b = 5.56$ Å (unique axis), $c \sin \beta = 46.5$ Å. Since the molecules would present small torsional angles between the adjacent thiophene rings, we expect in both monoclinic cases, different possible symmetries relating the two sublattices within an individual monolayer. The case of a 2_1 axis parallel to the unique axis ($b = 7.80$ Å) was found in a film deposited at room temperature.⁶

In this work, the X-ray analysis has been restricted to the meridional 00/ reflections in order to get the first structural data such as the monolayer thickness and in particular, the tilt angle of the molecular axes with respect to the c^* axis (normal to the monolayer (a,b) plane). For the highly oriented 6T films described here, the tilt value can be determined in first approximation, from the comparison between calculated and observed intensities of the 00/ reflections. The intensity fitting gives a tilt of 23° in the γ phase (22.42 Å thick monolayer). In the case of oriented dihexyl-substituted sexithiophene (α,ω -DH6T),⁷ we have found a long spacing of 35.6 Å and a tilt angle (of the 6T segments) of about 21° from the intensities of 00/ reflections. The great spacing of the high-temperature phase (δ phase) indicates a translation of 36.3 Å along the c^* axis. A preliminary interpretation could be given by assuming a unit cell extended to three monolayers instead of two, as commonly described in the crystal structures obtained at lower temperatures. Further investigation is required to get more insight on this complex structure. Nevertheless, the tilt angle is found close to 0° after the

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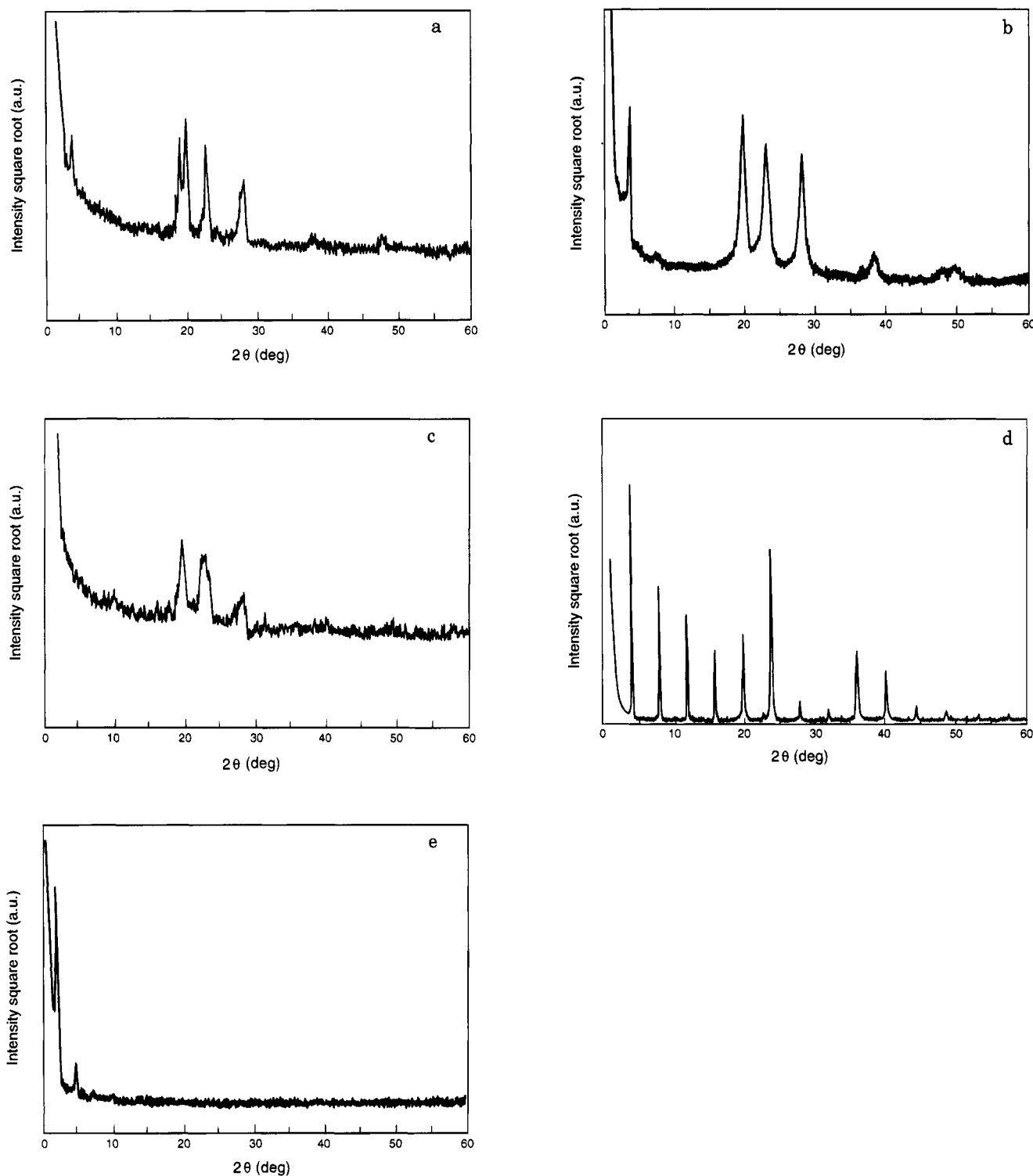


Figure 1. XRD spectra of 6T sexithiophene films deposited at various substrate temperatures (a) room temperature with a low deposition rate (1–5 Å/s), (b) room temperature with a high deposition rate (≈ 10 nm/s), (c) 77 K (no visible 00 l reflections), (d) 190 °C, and (e) 260 °C.

results of polarized UV–visible spectroscopy (see following section).

Polarized UV–Visible Spectroscopy. Figure 2 shows the nonpolarized absorption spectra at normal incidence of 6T and α,ω -DH6T deposited at room temperature. All spectra present a more or less intense hump at their low-energy side, followed by two or three less pronounced shoulders. This hump (located at 2.41 eV) and its accompanying shoulders are assigned to the π – π^* transition of the isolated planar molecule, and its

vibronic replica.^{8,11} It is red shifted as compared to the π – π^* transition in solution (around 2.85 eV), owing to the rigid all-trans planar conformation of the molecule in solid state, whereas in solution the thiophene rings are free to rotate around the inter-ring σ bonds. Importantly, α,ω -DH6T presents a narrow and intense absorption band at 3.39 eV which is not observed on

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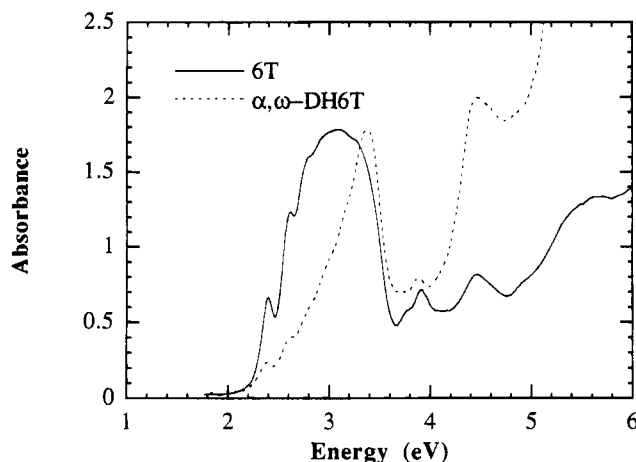


Figure 2. Absorption spectra of 6T (160 nm thick) and α,ω -DH6T (540 nm thick) films deposited at room temperature.

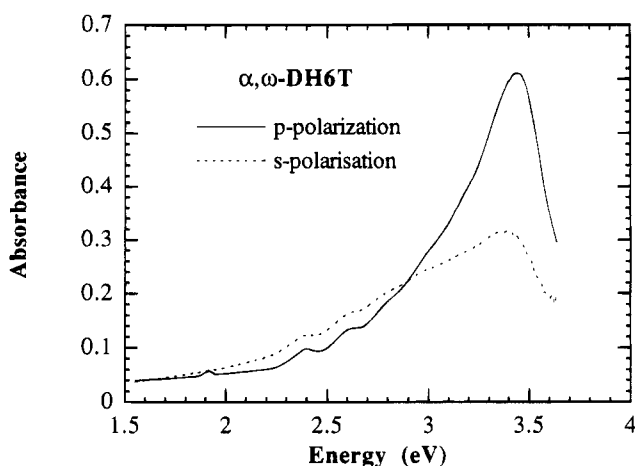


Figure 3. Absorption spectra of α,ω -DH6T under polarized light at an incidence angle of 80° . The electric vector oscillates parallel to the incidence plane in p polarization and normal to that plane in s polarization.

6T. Furthermore, the absorption spectra under polarized light, recorded at an angle of incidence of 80° (Figure 3) shows that this band is more intense when the electric field is parallel with the incidence plane (p polarization). The electric field associated to the optical wave oscillates parallel to the substrate plane in s polarization, whereas in p polarization, it contains both a component parallel and perpendicular to that plane. The presence of the narrow band in α,ω -DH6T and not in 6T confirms the preferential orientation of the substituted molecule roughly perpendicular to the substrate, even in thick films. As the long axis of the molecules stands close to the normal of the film, we can infer that this band is polarized along this long axis.

The effect of depositing unsubstituted 6T on a heated substrate is shown in Figure 4. As the temperature increases, the absorption in the visible range under s-polarized light decreases and the dichroic ratio increases. For a film deposited on a substrate at 285°C , the spectra strongly resemble those recorded by Egelhaaf and co-workers on monolayer films,⁸ and also those of the dihexyl-substituted 6T. The blue shift of the absorption band from 2.41 to 3.49 eV is characteristic of H aggregates and originates from exciton coupling of molecules having parallel transition dipoles. We note that such a hypsochromic shift has been reported almost

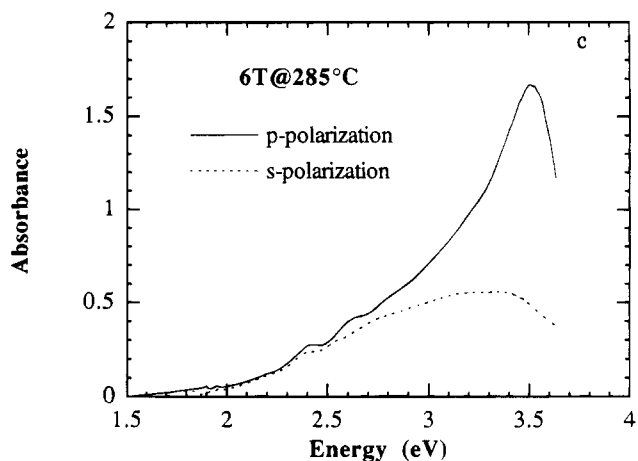
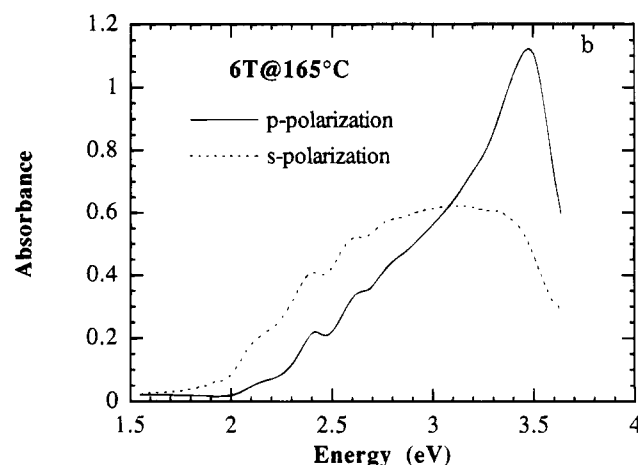
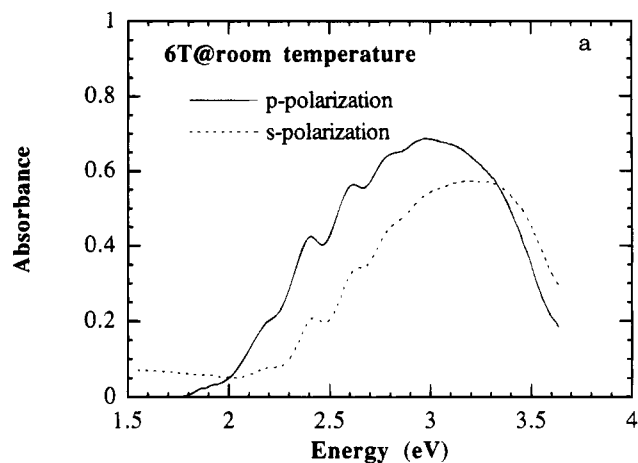


Figure 4. Same as Figure 3 for a 6T film deposited on a substrate at room temperature (a), 165°C (b), and 285°C (c).

30 years ago on Langmuir–Blodgett films of pure quinquethiophene.¹²

The tilt angle of the molecule might be obtained from the dichroic ratio A_p/A_s . Unfortunately, the high energy absorption peak under s polarization is completely hidden by a wide absorption band centered around 3 eV, the origin of which has not been ascribed to date.

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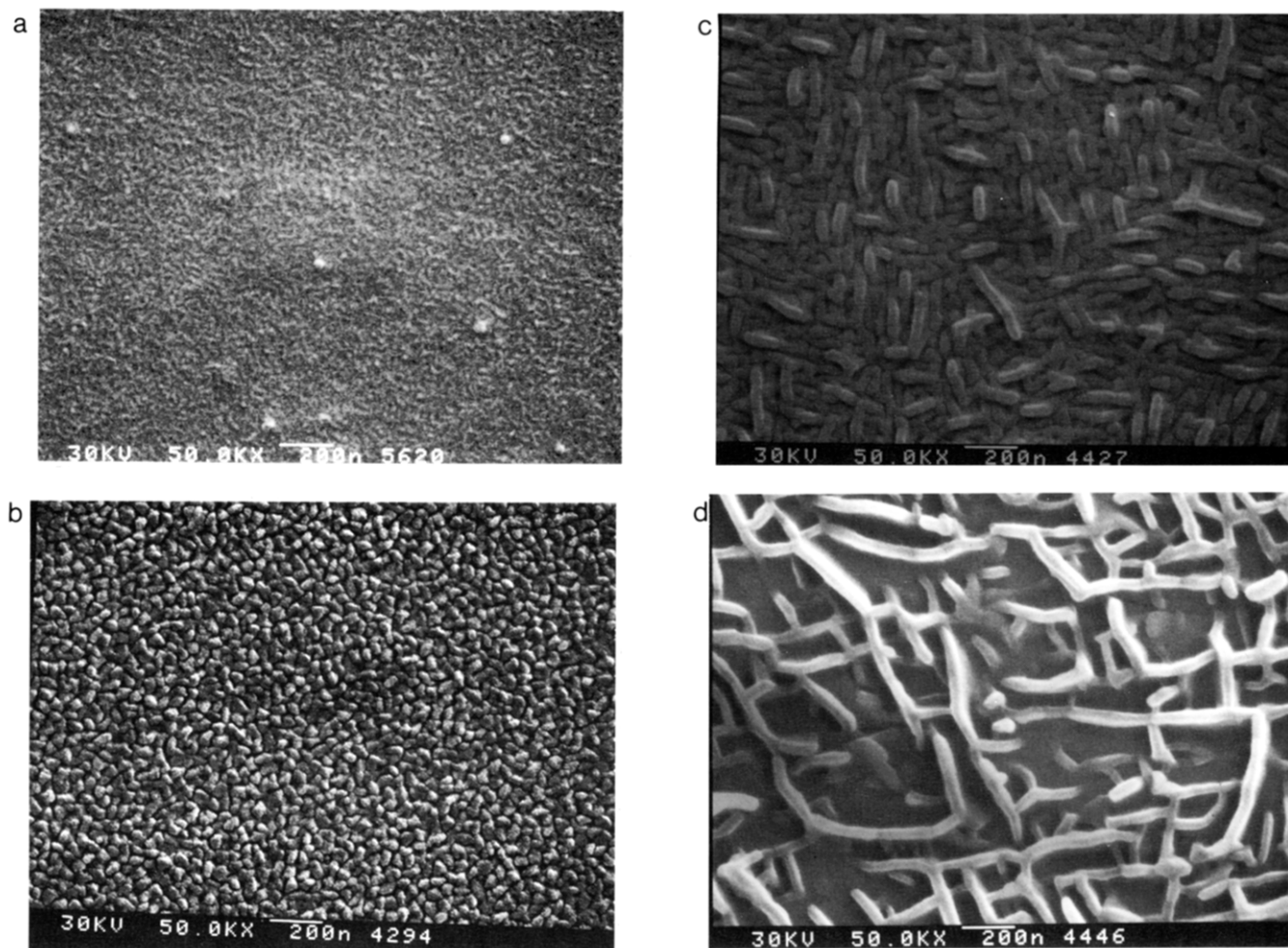


Figure 5. Plane view SEM observations of 100-nm-thick 6T films deposited at various substrate temperatures (a) 77 K (small grains of 10–30 nm), (b) room temperature (isotropic grains with diameter of 50 nm), (c) 190 °C (elongated grains of $30 \times 200 \text{ nm}^2$), and (d) 260 °C (50 nm wide lamellae connected with each other; magnification 50 000).

We note however that on α,ω -DH6T (tilt angle of 21°), the high-energy band is still observed under s-polarized light (Figure 3). This suggests that the tilt angle in unsubstituted 6T is close to 0° .

Scanning Electron Microscopy. SEM observation has been carried out to study the morphology of 6T thin films which depends on the substrate temperature and its influence on the mobility.

The 6T film deposited at 77 K presents a uniform surface consisting of small crystalline grains (10–30 nm) which results from a rapid condensation on a cold substrate (Figure 5a). In a deposition at room temperature (Figure 5b), we observe isotropic grains more or less separated from each other, with a more appreciable size (50 nm in diameter). Here, the different crystalline orientations with the molecules either parallel or perpendicular to the substrate (see XRD section) cannot be detected. In the 6T film deposited at 190 °C, the grains show an elongated shape with larger dimensions ($30 \times 200 \text{ nm}^2$) and align parallel and in close packing with the adjacent grains (Figure 5c). The grain alignment can extend at a large scale, which could favor an increase of the charge mobility. The 6T layer deposited at 260 °C shows a discontinuous surface arising from a possible cellular growth induced at high temperature (Figure 5d). Such a segregation process has been encountered in some complex cases of lamellar mor-

phologies and is reviewed in ref 13. It consists of larger lamellae (50 nm wide) with appreciable interlamellar spacings (up to several hundred nanometers). However, the grains are well connected with each other, giving rise to a network over the film surface, which leads to a further improvement of the electric charge transport.

The influence of the deposition temperature is clearly observed in the grain size and shape as well as in homogeneity and grain boundaries. Since a rapid nucleation takes place at low temperature, condensation results in a large number of small grains, leading to a uniform surface. The nucleation rate decreases at higher temperature whereas the lateral growth rate increases because of the high mobility of the adsorbed molecules. This gives rise to the growth of anisotropic grains with large lateral dimensions. Besides these general features, we give only a simple interpretation of the discontinuities occurring near the melting temperature. At these high temperatures, the number of nuclei is strongly reduced, and the grain shape and orientation are governed by surface free energy. As a result, the crystallites can develop laterally along one preferential growth axis, leading to the lamellar structure observed. The most outstanding effect would be the ability of the lamellar crystals to connect intimately

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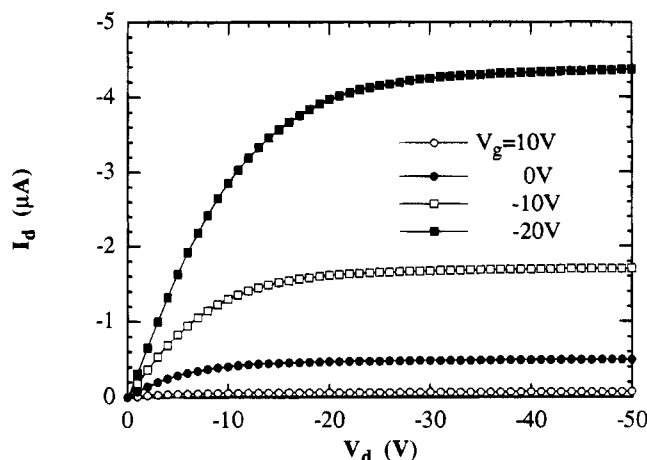


Figure 6. Drain current versus drain voltage characteristics for various gate voltages, measured on a 6T field-effect transistor. The insulator is spin-coated poly(methyl methacrylate) (PMMA).

Table 1. Conductivity and Field-Effect Mobility of 6T as a Function of the Substrate Temperature

substrate temp	μ_{FET} ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	σ_{\parallel} (S cm^{-1})	σ_{\perp} (S cm^{-1})
77 K	6×10^{-3}	6×10^{-4}	
room temp	2×10^{-3}	1.5×10^{-6}	2×10^{-7}
200 °C	9×10^{-3}	9×10^{-7}	
280 °C	2.5×10^{-2}	1.2×10^{-7}	4×10^{-9}

with each other at high temperature. This may be due to a coalescence of lamellae at the grain boundaries, providing a stable transition layer based on equivalent crystallographic planes or twinning planes in the new crystalline structure.

From the point of view of electric properties, the main differences appear in the lateral size and grain boundaries. Since the channel size in field-effect transistors (several micrometers) is much larger than the grain size of 6T films (a few hundreds of nanometers), the intrinsic mobility of a monocrystal cannot be presently accessed, and special attention could be paid to the grain boundaries on micrometric scale surfaces. According to X-ray analysis and SEM observation, we can expect that a high-temperature deposition would provide both suitable orientation and coalescence of the crystallites to enhance the field-effect mobility of 6T films.

Field-Effect Mobility. It is now well established that the field-effect mobility μ_{FET} of organic films can be accessed by measuring the current-voltage characteristic of insulated gate field-effect transistors. Figure 6 shows a set of drain current I_d vs drain voltage V_d curves of a sexithiophene based FET for various gate voltages V_g . μ_{FET} is calculated from the transconductance g_m at low V_d :

$$g_m = \partial I_d / \partial V_g = (W/L) \mu_{\text{FET}} C_i V_d$$

Here W and L are the channel width and length, respectively, and C_i the insulator capacitance.

The effect of the temperature of the substrate during the deposition of sexithiophene on the mobility is summarized in Table 1. The lowest value is observed on films deposited at room temperature. As we have shown previously, we obtain in that case a film with two orientations of the crystallites, one roughly perpendicular, and the other parallel to the substrate. When

6T is evaporated on a substrate held at liquid nitrogen temperature, we observe an increase of the mobility, from 2×10^{-3} to $6 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. This can be related to that nearly all the molecules lie flat on the substrate. An even greater increase of μ_{FET} is obtained when 6T is deposited on a heated substrate, where molecules tend to align along the normal to the substrate. For a substrate at 280 °C, a mobility of $2.5 \times 10^{-2} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ was measured, which approaches the value we have obtained with dihexyl-substituted sexithiophene.⁷

Table 1 also gives the conductivity of 6T films. The conductivity along the direction parallel to the film (σ_{\parallel}) was measured by the four-probe technique on films deposited on glass substrates, whereas the perpendicular conductivity (σ_{\perp}) is deduced from the current-voltage characteristics of Au-6T-Au sandwich structures. Heating the substrate results in a decrease of the parallel conductivity. As the mobility has increased, we can conclude that the concentration of dopants has been lowered. This reduction probably arises from the fact that a heated substrate tends to desorb any impurity that could deposit on it during the evaporation process. Such an interpretation is confirmed by the huge increase of the parallel conductivity we observe on films deposited on substrates held at the liquid nitrogen temperature. We have noted in that case some inhomogeneities of σ_{\parallel} measured at various points of the semiconducting film. Finally, we note that the anisotropy of the conductivity increases as the temperature of the substrate is raised. The ratio $\sigma_{\parallel}/\sigma_{\perp}$ which is less than 10 for a 6T film deposited at room temperature, raises to 30 in a film evaporated on a substrate at 280 °C. This again can be ascribed to the molecules being parallel to each others and perpendicular to the substrate.

Discussion

On the basis of correlated XRD, SEM analyses, UV-visible spectroscopy, and FET mobility measurements, it has been established that electric charge transport in 6T layers depends on crystal structure, orientation, and film morphology. According to the first X-ray data essentially given by 00 l reflections, various structures exist with fairly different molecular orientation ranging from 0° to 23° with respect to the c^* axis normal to the monolayer plane. Similarly, a tilt angle of 21° is found in dihexyl-substituted sexithiophene (α,ω -DH6T) taken as a reference material. It is clearly shown that the substrate must be heated at a high temperature in order to induce a complete 002 orientation of 6T crystals and thereby to improve significantly the FET mobility (μ_{FET}). However, the mobility measured in α,ω -DH6T films ($(3-5) \times 10^{-2} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) exceeds the values obtained in the highly oriented 6T films, independently of the molecular tilt angle. A comparable mobility is only achieved in the case of a 6T film deposited at 280 °C, but here the crystal structure differs appreciably from the usual model, and for this reason, we can assume the possible existence of various structures presenting a correct overlapping of π orbitals. On the other hand, the SEM observations show that the morphology of 6T films deposited at high temperature can also play a predominant role in electric charge transport. Despite the surface discontinuities associated with a cellular

growth observed near the melting temperature, the lamellar crystals can develop laterally along one crystallographic direction and connect intimately with each other, yielding a good quality of grain boundaries and a possible enhancement of the mobility. This could result from favorable molecular fluctuations as well as crystalline structure induced near the melting temperature.

Conclusion

We have studied the influence of substrate temperature on orientation, structure, and morphology of vapor deposited 6T films. Unsubstituted 6T can exist in four crystalline phases with different interlayer spacings

deduced from 00 l reflections by X-ray diffraction. The molecules are preferentially parallel to a cooled substrate (77 K) and stand up on a substrate heated at high temperature, leading to a complete 002 orientation near the melting point (≈ 290 °C). Although this adequate orientation contributes to an enhanced charge transport, the increase of the mobility is too small to be only accounted for by a better overlap of nearest-neighbor molecular orbitals. Instead, it is expected that the coalescence of the crystalline lamellae as observed by scanning electron microscopy, and the crystal structure in the high temperature phase (above 240 °C) could improve significantly the mobility of the 6T films, according to the electrical measurements performed on the field-effect transistors.