Oligophenyl-based organic thin film transistors

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Organic thin film transistors (TFTs) have been fabricated using thermally evaporated films of the oligophenyls *p*-quaterphenyl (*p*-4P), *p*-quinquephenyl (*p*-5P), and *p*-sexiphenyl (*p*-6P). The field-effect mobility of these TFTs ranges from 10^{-2} cm^2/V s for *p*-4P to 10^{-1} cm^2/V s for *p*-6P with on/off current ratio from 10^5 to 10^6. These values are comparable to those achieved using the more widely studied organic semiconductors alpha-sexithienyl (α-6T) and pentacene. X-ray diffraction reveals a high degree of molecular ordering, believed to be important for obtaining high field-effect mobility in organic TFTs. © *1997 American Institute of Physics.* [S0003-6951(97)04552-X]

The potential advantages of organic over conventional thin film transistor (TFT) materials like hydrogenated amorphous silicon (*a*-Si:H) include lower processing cost and low temperature processing compatible with plastic substrates, which may allow mechanically rugged and flexible systems. The active matrix liquid crystal display (AMLCD) is one example where organic-based TFTs may find use as pixel control elements.

While organic materials with conductivities ranging from metallic to insulating have been demonstrated, most of these materials do not have electrical properties suitable for use as active layers in organic TFTs. It has only been within the last decade that organic-based field-effect devices have begun to yield results in the range of interest for electronic applications. Using the short-chain thiophene oligomer alpha-sexithienyl (α-6T), Garnier *et al.* fabricated metal insulator semiconductor field-effect transistors with field-effect mobility of 2.7×10^{-2} cm^2/V s.[1] Thermally evaporated thin films of *a*-6T show strong molecular ordering on a long-range scale which may be the reason for the observed increased mobility compared to values typically obtained for TFTs fabricated using, for example, solvent-cast polythiophene films. Subsequent work on α-6T-based TFTs fabricated using SiO$_2$, poly(methylmethacrylate) (PMMA), or similar gate dielectric materials have yielded TFTs with field-effect mobility as large as 5×10^{-2} cm^2/V s and on/off current ratios of 10^6.[2–4]

TFTs fabricated using the short-chain molecule pentacene as the active layer have a performance comparable to *a*-Si:H TFTs.[5] Recently we reported on pentacene-based TFTs with field-effect mobility and on/off current ratio as large as 1.5 cm^2/V s and 10^8, respectively.[6] Like α-6T, thermally evaporated pentacene thin films show strong molecular ordering.[7–9]

While the reported values for α-6T and pentacene-based TFTs are encouraging it is not clear that these materials are the best choices for organic-based TFTs. It is likely that processing simplicity and reproducibility may determine the material choice. We report here on another small-molecule system with relatively high field-effect mobility and on/off current ratio. We have fabricated organic-based thin film transistors using vacuum-deposited active layers of the oligophenyls: *p*-quaterphenyl (*p*-4P), *p*-quinquephenyl (*p*-5P) and *p*-sexiphenyl (*p*-6P), with performance similar to oligothiophene or pentacene-based TFTs. These oligophenyls may be of interest because of their particularly high thermal stability and possible chemical compatibility with the processing required for integrated organic devices.

For the oligophenyl-based TFTs described here, a heavily doped silicon wafer is used as a substrate, and a 400 nm thermal oxide is grown for use as the gate dielectric. All TFTs were fabricated using vacuum evaporated films of as-purchased oligophenyl material (Aldrich or TCI). The active layers are deposited in a system dedicated to organic material deposition with a background pressure less than 7×10^{-5} P. The devices are completed by evaporating gold through a shadow mask to form source and drain contacts, and the gate contact is made to the wafer backside. The TFTs have a channel length and width of 20 and 540 μm, respectively.

Figure 1 shows drain current (I_D) versus drain-to-source voltage (V_{DS}) for several values of gate voltage (V_G) for a *p*-4P active-layer TFT. The *p*-4P active layer has an average thickness of 23 nm and was deposited onto a substrate held at 130 °C. From the $\sqrt{I_D}$ vs V_G characteristics we extract a field-effect mobility of 1×10^{-2} cm^2/V s for the device shown in Fig. 1. The mobility is extracted for the TFT biased in the saturation region with $V_{\mathrm{DS}}=-100$ V for this and all the organic TFTs reported here. This device has an on/off current ratio greater than 10^5.

The I_D vs V_{DS} characteristics of a *p*-5P-based TFT are shown in Fig. 2. The substrate was held at 100 °C during the deposition of the 50 nm thick active layer. The field-effect mobility is 4×10^{-2} cm^2/V s and the on/off current ratio is greater than 10^6.

Figure 3 shows the I_D vs V_{DS} characteristics for a *p*-6P-based TFT with an average active layer thickness of 50 nm. The *p*-6P film was deposited onto a substrate held at 200 °C. This *p*-6P-based TFT has a field-effect mobility of

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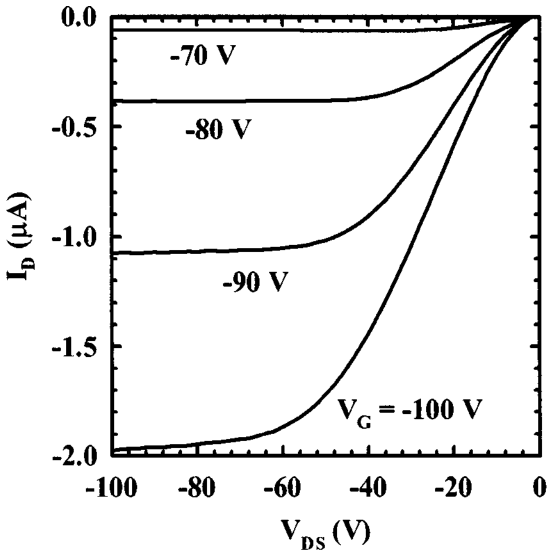

FIG. 1. The I_D vs V_{DS} characteristics of a p-quaterphenyl TFT.

7×10^{-2} cm^2/V s and an on/off current ratio greater than 10^6.

Interestingly, sexiphenyl was considered previously as an active material for organic-based TFTs, but was not found to yield working devices.[10] We believe the most significant factor in obtaining the mobility reported here is the quality of the active layer. We expect that carrier transport in field-induced channels in oligophenyl-based TFTs is dominated by the difficulty of moving carriers from one molecule to the next because of disorder and chemical impurities which can form trapping states. Thus a high degree of molecular ordering in the active organic material may be necessary for high-mobility devices.

The oligophenyl-based TFTs are well-behaved square-law devices and the fitting line used for mobility extraction fits the data over a wide range of gate voltage. Although working devices were obtained using oligophenyl active layers deposited on substrates held at room temperature, devices fabricated using substrates held at or above 100 °C showed improved performance. For all three materials, the extracted threshold voltage is greater than −45 V, which may explain the previously reported results for p-6P-based TFTs where no field effect was observed. Presently, these large threshold

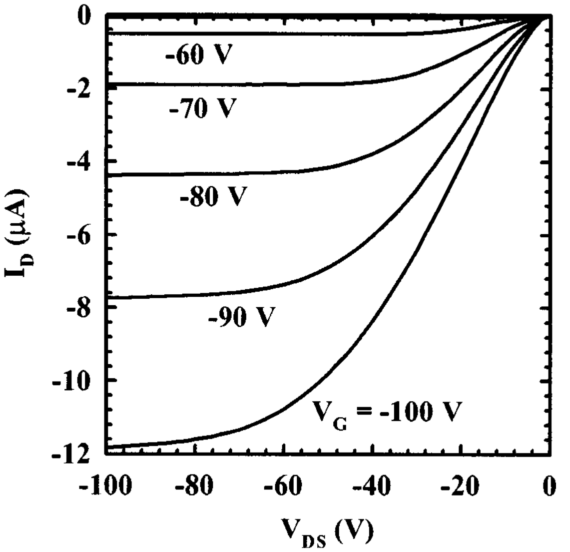

FIG. 2. The I_D vs V_{DS} characteristics of a p-quinquephenyl TFT.

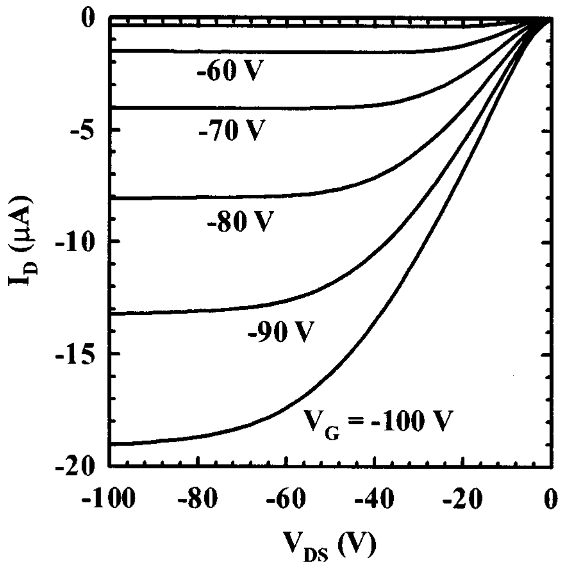

FIG. 3. The I_D vs V_{DS} characteristics of a p-sexiphenyl TFT.

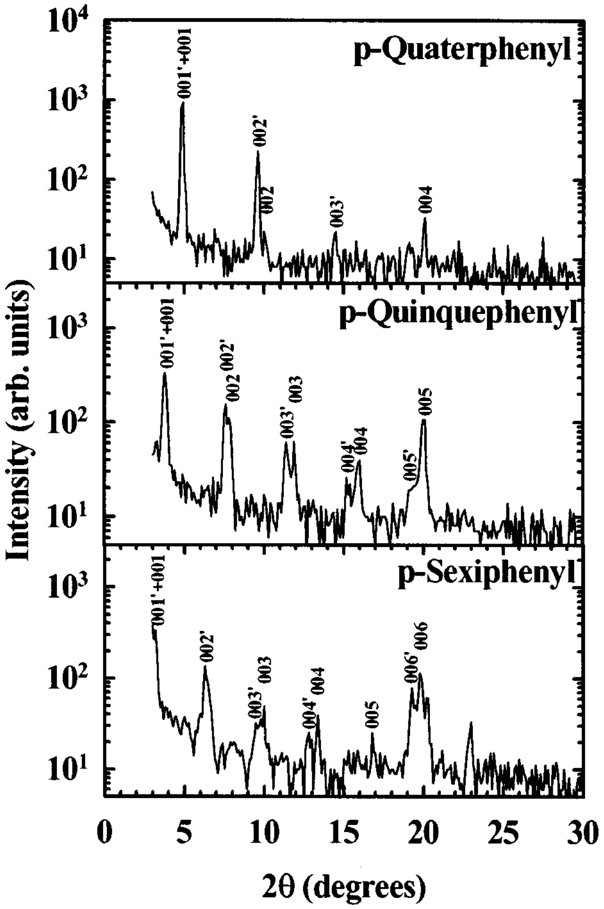

FIG. 4. θ-2θ x-ray diffraction patterns of (a) p-quaterphenyl, (b) p-quinquephenyl, and (c) p-sexiphenyl films with average thickness of 50 nm deposited onto thermally oxidized silicon wafers held at room temperature.

TABLE I. The single crystal d_{001} spacing and the extracted d_{001} and $d_{001'}$ spacings for the two families of peaks in Figs. 4(a)–4(c).

	d_{001} spacing		
Oligophenyl	$d_{001\ \mathrm{single\ crystal}}$ (Å)	d_{001} (Å)	$d_{001'}$ (Å)
p-4P	17.71	17.7±0.2	18.6±0.2
p-5P	21.98	21.8±0.2	22.8±0.1
p-6P	26.22	26.2±0.4	27.6±0.5

voltages make oligophenyl-based TFTs unsuitable for low voltage applications. However, we have shown in previous work using pentacene as the active material that threshold voltage can be varied over a wide range by controlling the interface properties between the active layer and the gate dielectric.[6]

The relatively large on/off current ratio of 10^5-10^6 obtained for p-4P-, p-5P-, and p-6P-based TFTs was achieved using as-purchased material. As shown previously for α-6T and pentacene-based TFTs, purification of the starting materials may lead to improved on/off current ratio in these oligophenyl-based TFTs.[3,5] Additionally, Figs. 1–3 all show evidence of significant contact effects which limit the extracted values of field-effect mobility.

To investigate the molecular ordering present in these oligophenyl active layers, x-ray diffraction was used. The diffraction vector was aligned perpendicular to the substrate surface. Figures 4(a)–4(c) show θ-2θ scans of p-4P, p-5P, and p-6P films deposited by thermal evaporation onto oxidized silicon substrates held at room temperature. These oligophenyl thin films show strong molecular ordering even when deposited at room temperature. For all three oligophenyls, the peaks labeled 00_l are in close agreement with the calculated d_{00_l} spacings of the single crystal oligophenyls, while the peaks labeled $00_l'$ have elongated d_{00_l} spacings and correspond to a thin film phase.[11,12] Note that these $00_l'$ peaks cannot be explained by any hk_l peaks of single crystal oligophenyls. Like previous authors, we attribute these $00_l'$ peaks to oligophenyl thin film phases with structural parameters slightly distorted from those found in single crystals of these phases (e.g., a different monoclinic angle β).[13,14] These results show the films are oriented with the long axis (c axis) of the molecule nearly perpendicular to the substrate surface. Table I lists the calculated single crystal d_{001} spacing and the extracted d_{001} and $d_{001'}$, spacing for the two families of peaks in Figs. 4(a)–4(c).

Oligophenyl films deposited onto substrates held at elevated substrate temperatures show improved molecular ordering, with the majority peaks now corresponding to the single crystal phase. This is shown in Fig. 5 for a p-4P film deposited onto an oxidized silicon wafer held at 90 °C. The majority peaks and minority peaks have d_{001} spacings of 17.7 and 18.6 Å, respectively. This trend is also observed for p-5P and p-6P films deposited onto substrates held at elevated temperatures. It is notable that for all three oligophenyl-based TFTs, higher substrate temperatures also yielded improved device performance.

The x-ray diffraction patterns of the oligophenyl films show strong similarities to x-ray diffraction patterns of pentacene thin films deposited onto oxidized silicon substrates. Pentacene also forms well ordered films with the long axis (c axis) of the pentacene molecule nearly perpendicular to the substrate surface.[9] Additionally, both a single crystal film phase and a thin film phase are present in pentacene films deposited onto substrates held at elevated temperatures.[7,8]

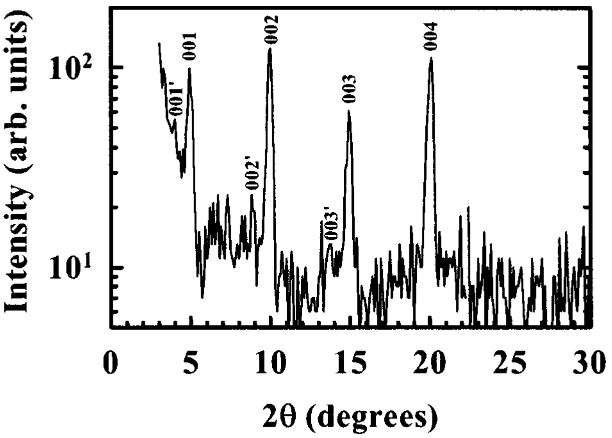

FIG. 5. θ-2θ x-ray diffraction pattern of a p-quaterphenyl film with an average thickness of 50 nm deposited onto a thermally oxidized silicon wafer held at 90 °C.

Organic-based TFTs using oligophenyls as the active material. These devices show relatively high field-effect mobility ($10^{-2}-10^{-1}$ cm^2/V s) and on/off current ratio (10^5-10^6). In addition, oligophenyl thin films are strongly ordered, even when deposited onto amorphous substrates held at room temperature. While working TFTs were fabricated using oligophenyl active layers deposited onto substrates held at room temperature, TFTs fabricated using active layers deposited at elevated substrate temperatures showed improved performance.

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