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Field effect transistors based on poly(3-hexylthiophene) at different length scales

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Abstract
In this paper we report on thin film transistors based on drop casting solutions of regioregular poly(3-hexylthiophene) (P3HT) over prefabricated gold electrodes. This polymer is known to self-organize into a lamellar structure in chloroform resulting in high field-effect mobilities. We studied the dependency of the charge carrier mobility of devices prepared from solution in chloroform with electrode spacings ranging from 5 μm to 20 nm. It was found that the overall trend was that the mobility decreased as the electrode spacing was made smaller, indicating that the transport properties on closely spaced electrodes were dominated by the contacts. Applying an ac voltage during the preparation of such films resulted in lower mobilities. However, P3HT in *p*-xylene forms fibres, which were aligned between the electrodes by applying an ac field. Films of aligned fibres with mobilities as high as 0.04 cm^2 V^{-1} s^{-1} were prepared.

1. Introduction

Conducting polymers that are soluble and processible are potentially useful for building inexpensive and flexible electronic devices. Poly(3-alkylthiophenes) have been found to have many potential applications such as light emitting diodes, non-linear optical devices, rechargeable batteries, and field-effect transistors (FETs) [1, 2]. In particular, regioregular poly(3-hexylthiophene) (P3HT) has attracted a great deal of interest as it has the highest reported field-effect mobility in polymer FETs so far, 0.1 cm^2 V^{-1} s^{-1} [3].

Typically, solution processed polymers form complex microstructures, where microcrystalline domains are embedded in an amorphous matrix [4]. The disordered matrix limits the charge transport resulting in low field-effect mobilities. P3HT forms two different types of microstructures depending on the solvent that is used. When P3HT is deposited from a chloroform solution, the polymer self-organizes into a lamellar structure [3, 5]. The highest mobilities for P3HT are measured for this structure. This is due to the high degree of crystallinity and strong interchain interactions. Charge transport in these polymer FETs depends strongly on the orientation of the crystalline domains as well as the size of the crystallites. The optimal orientation corresponds to the plane of the conjugated rings being perpendicular to the transport direction. Scanning tunnelling microscope studies show that the typical size of crystallized domains is of the order of 10–20 nm [6, 7].

When *p*-xylene or cyclohexanone are used as solvents, P3HT forms fibres in the solution, which can then be deposited on the substrate [8]. Hole mobilities up to 0.06 cm^2 V^{-1} s^{-1} have been reported very recently for single nanofibres [9]. The formation of similar fibres has been observed in other conjugated polymers and is believed to be governed by the π-stacking of the conjugated chains [10].

Here we describe measurements on P3HT thin film transistors deposited from both chloroform and *p*-xylene. Electrodes were used with gaps in the range from 5 μm to

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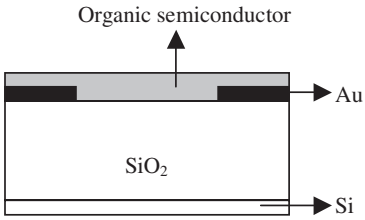

Figure 1. The device configuration used.

20 nm. Very small gap sizes were used in the hope that the electrodes would be bridged by well-ordered regions. In some of the experiments an ac voltage was applied across the electrodes during the deposition of P3HT in an attempt to induce ordering in the polymer.

2. Experimental procedure

Regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT) was obtained from Aldrich, dissolved in chloroform and treated with a few drops of hydrazine to reduce oxidized segments in the polymer. After washing with water, the chloroform layer was dried with magnesium sulfate and evaporated to dryness. The residue was Soxhlet extracted first with dichloromethane to remove the low molecular weight fractions and subsequently with chloroform to obtain the high molecular weight fraction. After precipitation with methanol, an amorphous solid was obtained. Gel-permeation chromatography (GPC) analysis, performed on a Waters 590 GPC using chloroform as solvent and a PL gel column calibrated with polystyrene standard, yielded a molecular weight of Mw $=$ 99.000 g mol^{-1} and a polydispersity of PD $= 3$.

Figure 1 shows the configuration used, which is a bottom-contact device with the organic semiconductor deposited onto the gate insulator and the prefabricated source and drain electrodes. The fabrication of the contacts was carried out using electron-beam lithography and a double resist layer of poly(methyl methacrylate) (PMMA) on an oxidized silicon wafer ($t_{ox} \approx 200$ nm thick SiO_2). Ti/Au electrodes were evaporated at liquid nitrogen temperature to ensure a smooth surface. In order to get electrodes with small gaps, a shadow evaporation technique was used. Using this technique, it is possible to adjust the spacing between the electrodes between 5 and 100 nm. Two microlitre drops of a solution of 1 mg ml^{-1} of P3HT in chloroform were drop cast on the electrodes as a semiconductor layer. In order to get fibril structures, solutions of 0.25–0.5 mg ml^{-1} of P3HT in *p*-xylene were used.

The transport measurements of these devices were carried out at room temperature in a microscope probe station under flowing nitrogen coupled to a battery powered data acquisition system. To promote the ordering of the polymer, an ac voltage (1.0–2.0 V, 102 kHz) was applied to the gold electrodes during the evaporation of the solvent.

The devices were inspected by atomic force microscopy using a DI 3100 (Veeco) AFM in tapping mode, and scanning electron microscopy images were taken in an XL30 SFEG SEM.

3. Results

3.1. Calculation of charge carrier mobilities

When P3HT films were deposited over metal source and drain electrodes, the measured current that flowed between the electrodes was a linear function of the applied voltage, and the devices could be characterized by a linear resistance. This resistance was a function of the gate voltage, and decreased as a more negative gate voltage was applied. This is typical behaviour for a p-type semiconductor where the majority charge carriers are holes. One measure of the quality of the devices is the charge carrier mobility [11]. The formula for the mobility is

$$\mu = \frac{\partial^2 I_{SD}}{\partial V_{SD}\,\partial V_G}\frac{L}{CW}.$$

Here μ is the mobility, I_{SD} is the source–drain current, V_{SD} is the source–drain voltage, V_G is the gate voltage, W is the width of the semiconducting channel, L is the length of the channel, and C is the capacitance per unit area of the gate, calculated as ($C = \varepsilon(SiO_2)\varepsilon_0/t_{ox}$). The expression for the mobility neglects the influence of contact resistances and charge traps in the gate oxide. Consequently it merely provides a lower limit on the device mobility, and not the intrinsic mobility of the material [12].

The mobility of the films was measured using two kinds of electrodes: interdigitated electrodes and point electrodes. These two kinds of electrodes are shown in figure 2. The electric field lines in the interdigitated electrodes run perpendicular to the electrodes, and fringing fields can be neglected. Since the width of the electrodes and the length of the gap are known, it is then straightforward to calculate the mobility for this geometry. However, it is not possible to fabricate interdigitated electrodes with very small electrode spacings. The point electrodes were made with spacings of 5, 1 μm, 250, and 20 nm. These electrodes can be spaced more closely than the interdigitated electrodes but the electric field pattern is more complex for the point electrodes. By first comparing measurements between the interdigitated electrodes with a 5 μm gap and the point electrodes with a 5 μm gap, we were able to determine that the point electrodes corresponded to interdigitated electrodes with a gap length to electrodes width of $L/W = 0.8$. Since all of the point electrodes have the same shape (figures 2(b)–(d)), the electric field pattern should have the same shape for all of the point electrodes, and we used the parameter $L/W = 0.8$ to calculate an approximate mobility for all of the point electrodes. Although the current is concentrated between the two points for the point electrodes, the current depends weakly on the size and the shape of the polymer that was drop cast onto the electrodes. This resulted in some scattering in the mobility measurements.

3.2. Nanoscale P3HT FETs

Figure 3 shows the electrical characteristics a P3HT film formed by drop casting 2 μl of a solution of 1 mg ml^{-1} of P3HT in chloroform on point electrodes with a spacing of 1 μm. The resistance of the film changed as different gate voltages V_G were applied to the silicon substrate, which acted as a gate. The mobility of this device was 0.024 cm^2 V^{-1} s^{-1}.

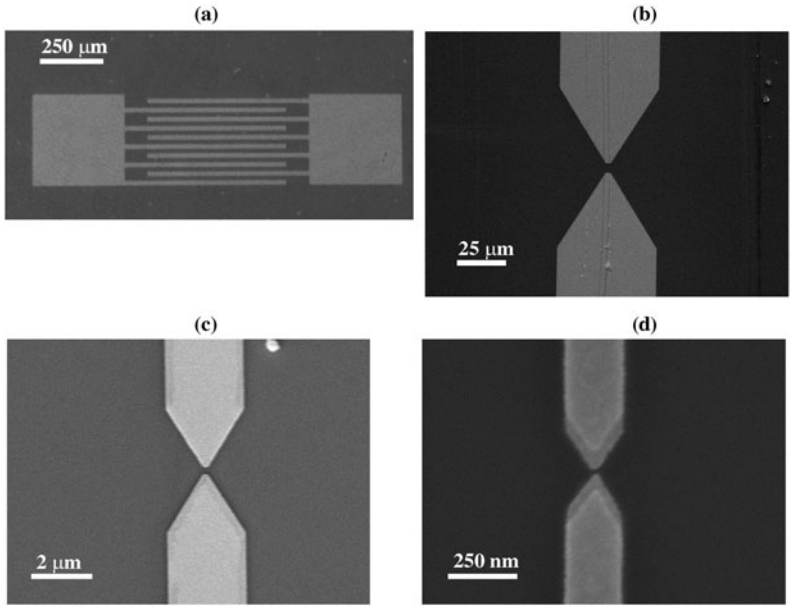

Figure 2. SEM images of the electrodes. (a) Ten interdigitated electrodes of width 600 μm and spacing 20 μm. (b)–(d) Self similar point electrodes with gaps of 5 μm, 250 nm and 20 nm, respectively.

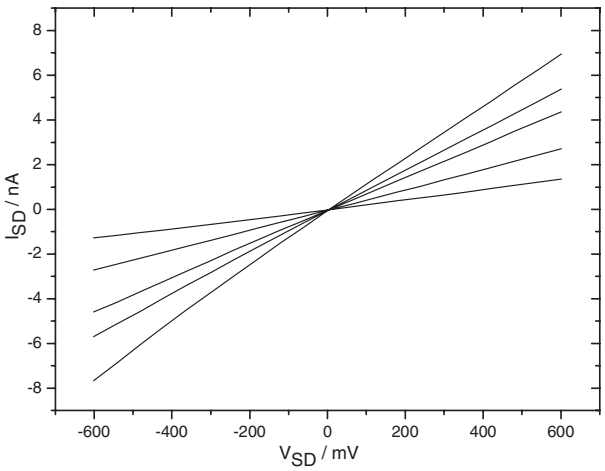

Figure 3. Source–drain current versus source–drain voltage at gate voltages (curves from top to bottom on the right-hand side of the graph) −40, −30, −20, −10, and 0 V for a P3HT thin film transistor deposited from a chloroform solution on 1 μm spaced point electrodes.

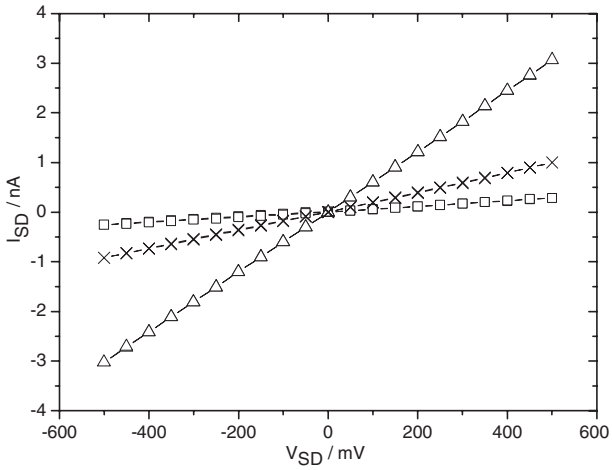

Figure 4. I–V characteristics of a P3HT film FET with gold electrodes spaced 20 nm from each other just after preparing the film (-□-), after exposing it to air for 24 h (-△-), and after applying a gate voltage of −40 V for 15 min to the air exposed sample (-×-).

All of the P3HT transistors were very sensitive to oxygen, humidity, and light. Figure 4 shows the I–V characteristics of a P3HT film immediately after preparation and after 24 h in the air. The resistance of the sample exposed to air diminishes due to the oxidation of the polymer which induces more charge carriers. However, applying a negative gate voltage of −40 V causes the resistance to increase again. We believe that the negative gate voltage reduces the polymer, thereby decreasing the number of charge carriers. Often applying large gate voltages such as this leads to charge trapping. We cannot rule this out entirely but a negative gate voltage should result in negative trapped charge that would increase the number of positively charged mobile holes. The decrease in the mobility when a negative gate voltage is applied implies therefore that the gate is predominately reducing the film.

In order to avoid the effect of oxygen doping in the study of the transport properties of the devices, the measurements were taken immediately after drop casting the films from freshly prepared solutions and under flow of nitrogen. The I–V curves were quickly registered in the dark, always starting by applying the most negative gate voltage to reduce the polymer completely.

Figure 5 shows the mobilities as a function of the electrode spacing. All of these films were deposited from a chloroform solution. There is a large variation in the mobility measurements, which may be due to the high anisotropy of the films. The anisotropy of poly(alkylthiophenes) has previously been studied, and it was reported that for samples drop cast from solvents with low boiling points the anisotropy tends to be higher [13]. For devices with channel lengths of 5 and

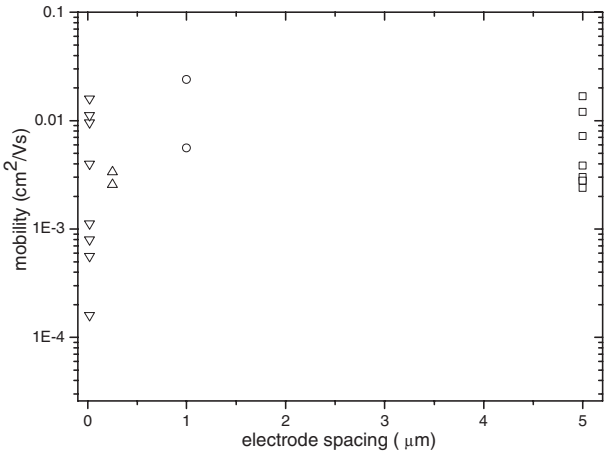

Figure 5. Mobility versus electrode spacings of P3HT thin films transistors prepared by drop casting P3HT from chloroform solutions.

1 μm, mobilities of the order of 0.02–0.01 cm^2 V^{-1} s^{-1} were obtained, which is in agreement with results found in the literature when the lamellar domains are perpendicular to the substrate [14–16]. For smaller gaps of 20 nm, a quite wide range of mobilities were found, but they were often one order of magnitude smaller, 0.004–0.001 cm^2 V^{-1} s^{-1}. The overall trend seems to be that the mobility decreases as the electrode spacing is made smaller, which might indicate that for small electrode spacing the mobility is limited by the contacts, not by transport through the polymer itself. However, with the smaller electrode spacing a larger scatter in the mobilities is found, suggesting that parameters such as the anisotropy of the film or the contacts affect much more the mobility when using these small gaps.

3.3. Application of an ac voltage during the film preparation

The application of an ac voltage across the electrodes is known to trap conducting nanoparticles from solution [17] and to align conducting fibres along the direction of the applied electric field. The applied field induces a dipole in conducting elements and pulls them towards the region where the field gradient is the highest. This technique has been successfully applied for aligning nanotubes and nanowires [18–21].

When an ac voltage (1–1.5 V, 102 kHz) was applied across electrodes spaced at 20 nm while P3HT was deposited from chloroform, the resulting films had very high resistances, giving mobilities of the order $\sim 10^{-4}$ cm^2 V^{-1} s^{-1}. Instead of promoting better ordering of the films, applying an ac field significantly decreased the mobility. It is known that the mobility of P3HT grown from chloroform depends on the orientation of the lamellar domains [3]. We speculate that the ac voltage either inhibited the formation of the lamellar structures or caused the domains to form with the less favoured orientation for producing high mobilities.

P3HT fibres deposited on the electrodes from *p*-xylene without applying any field are shown in figure 6(a). An ac voltage was also applied to the electrodes while depositing P3HT from *p*-xylene. Figure 6(b) shows an AFM image of P3HT fibres aligned between gold electrodes 500 nm apart after

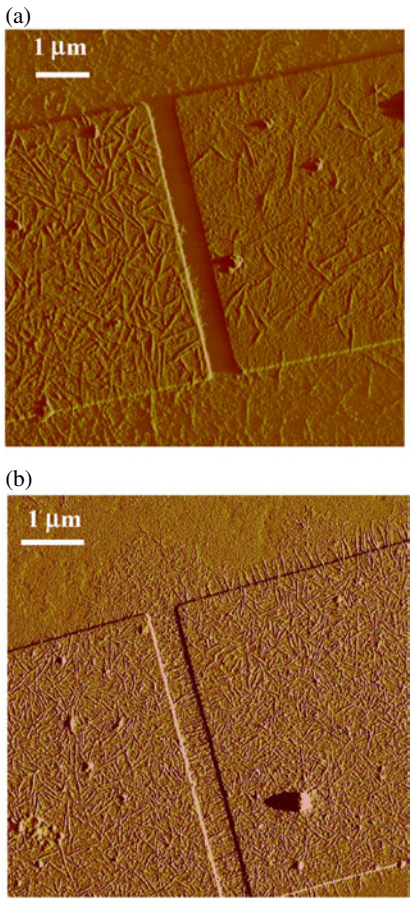

Figure 6. An AFM image of a device prepared by drop casting a solution of P3HT in *p*-xylene (a) without applying any field and (b) applying an ac voltage (2 V, 102 kHz) on the right electrode of the image. This resulted in the formation of aligned nanofibres. (This figure is in colour only in the electronic version)

drop casting 5 μl of a diluted solution of P3HT in *p*-xylene. The applied field clearly aligned the fibres between the electrodes. The applied voltage had an amplitude of 2 V and a frequency of 102 kHz. In accordance with previous work [9], the fibres typically have a height of 3–7 nm and lengths 0.5–2 μm.

To make a well-defined measurement of the mobility through the aligned fibres, P3HT was deposited from *p*-xylene on interdigitated electrodes 600 μm wide and spaced 2 μm apart. An ac voltage of 2 V with a frequency of 102 kHz was applied during the deposition, which resulted in fibres depositing mainly between the electrodes and not on the gold pads. Figure 7 shows the source–drain current I_{SD} as a function of the applied source–drain voltage V_{SD} across the two gold electrodes for different gate voltages V_G applied to the silicon substrate. A mobility of 0.04 cm^2 V^{-1} s^{-1} was obtained for these devices. This is of the order of the highest mobility reported for single nanofibres [9].

4. Summary

Thin films transistors based on drop casting solutions of P3HT have been studied. These films are known to be very

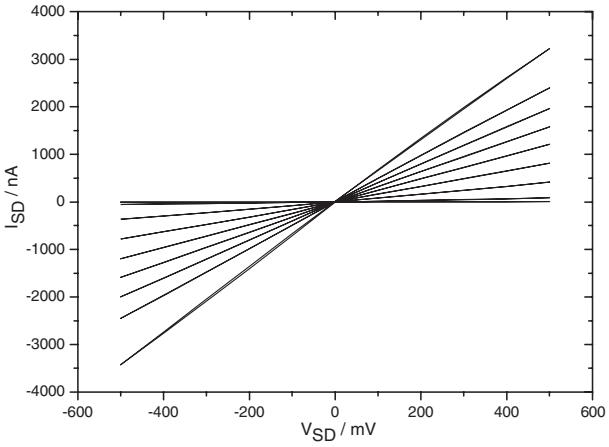

Figure 7. Source–drain current versus source–drain voltage at gate voltages (curves from top to bottom on the right-hand side of the graph) −40, −35, −30, −25, −20, −15, −10, −5 and 0 V for a P3HT thin film of aligned fibres.

sensitive to air, which causes the oxidation of the polymer. However, it has been seen that by applying a negative gate voltage the polymer can reversibly return to its reduced form. The measurements of the devices prepared from solutions in chloroform using different gap sizes show that the transport properties on closely spaced electrodes are affected by the contacts and the anisotropy of the films. Applying an ac voltage during the preparation of such films resulted in lower mobilities. Nevertheless, the ac field is very useful to align the P3HT nanofibres that are formed in *p*-xylene. This has produced films of aligned fibres with mobilities as high as 0.04 $cm^2\ V^{-1}\ s^{-1}$.

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