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Organic Electronics 3 (2002) 105–110

Organic Electronics

www.elsevier.com/locate/orgel

Dependence of field-effect hole mobility of PPV-based polymer films on the spin-casting solvent

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Received 11 January 2002; received in revised form 5 March 2002; accepted 28 June 2002

Abstract

We present field-effect mobility measurements on a conjugated polymer poly(2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene) (MDMO-PPV) that was spin-cast from different solvents. The organic field-effect transistors were fabricated using an Al/p$^+$-Si/SiO$_2$/TiW/Au/MDMO-PPV configuration. The hole field-effect mobilities for MDMO-PPV deposited from a toluene and chlorobenzene solution were found to be 5×10^{-6} and 3×10^{-5} cm^2/(V s), respectively, as calculated from the saturation regime. These results are explained on the basis of a modification of the polymer morphology caused by using different solvents, as evidenced by light scattering experiments on the MDMO-PPV solutions.

PACS: 72.80.Le; 73.61.Ph
Keywords: Field-effect transistor; Conjugated polymer; PPV; Mobility; Solvent; Morphology

1. Introduction

Conjugated polymers have proven their potential for the use in a wide range of optoelectronic applications. Most of the research efforts made to improve device performances have mainly focussed on screening different candidate materials. However, it has recently been shown that controlling the film morphology of a given conjugated polymer can also have a remarkable influence on the final device properties [1]. Along with effects such as the modification of charge transfer and energy transfer processes that take place within the polymer layer itself, the contact resistance at the polymer/electrode interfaces can also be manipulated by changing the molecular morphology. In the next paragraph these phenomena will be addressed in more detail.

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1566-1199/02/$ - see front matter
PII: S1566-1199(02)00039-3

It is generally accepted that *charge* transport along one polymer chain is a fast process. Measurements of one-dimensional intrachain mobilities of holes and electrons in dilute solutions of poly(2-methoxy-5-[2′-ethyl-hexyloxy]-1,4-phenylene vinylene) (MEH-PPV) yielded 0.2 and 0.5 $cm^2/V\,s$, respectively [2]. However, interchain transport relies on the hopping process, and measurements of charge carrier mobilities in films of MEH-PPV typically yield values four orders of magnitude lower than the on-chain mobilities. In contrast, it has been demonstrated that interchain *energy* transfer occurs two orders of magnitude faster than intrachain exciton migration in MEH-PPV [3]. Thus, it is clear that the optical and electronic properties of a bulk conjugated polymer medium are strongly affected by the morphology. In particular, it has been shown that the photoluminescence (PL) spectrum of MEH-PPV films spin-cast from chlorobenzene (CB) is red-shifted with respect to that of MEH-PPV films spin-cast from tetrahydrofuran (THF), reflecting the increase of the interchain interactions in CB-cast films as compared to THF-cast films [3,4]. This increase is attributed to the higher number of chromophore aggregates of MEH-PPV chains in aromatic solvents such as CB, in which the polymers exhibit a higher conjugation length because of these two-dimensional interchain aggregates. As a result, MEH-PPV films cast from CB possess a more efficient interchain charge transport than films deposited from a non-aromatic solvent such as THF. Similarly, in THF-cast MEH-PPV the PL efficiency is enhanced due to the presence of a larger number of recombination centers. However, the turn-on voltage for light emission of dichlorobenzene-cast MEH-PPV LEDs was found to be smaller than in the case of THF-cast MEH-PPV LEDs [5]. This discrepancy was explained by the improved hole injection at the anode/polymer (PEDOT/MEH-PPV) interface when using CB as solvent. In that work a Ca/Al bilayer was used as top contact, making the injected electrons the majority carriers. Therefore a molecular reorganization at the polymer/cathode interface could be ruled out as reason for the solvent dependent LED performance. Nguyen et al. found that annealed THF-cast MEH-PPV films in an ITO/MEH-PPV/Mg:Ag/Ag configuration showed a higher EL efficiency than as-cast THF MEH-PPV films [4]. Here, an enhanced electron injection from the cathode, resulting from a smoother interfacial contact, was suggested.

Field effect transistor (FET) mobilities of conjugated systems are also limited by the π–π interchain interactions of neighboring polymer chains. Charge modulation spectroscopy has revealed that the contribution of charge transfer transitions becomes stronger with increasing regioregularity of poly(3-hexylthiophene) (P3HT), thus resulting in higher mobility values [6]. Moreover, treatment of the SiO_2 with hexamethyldisilazane promotes the self-organization of the P3HT polymer chains. In this way the hole mobilities of P3HT reach values up to 0.1 $cm^2/V\,s$ [7,8]. A dependence of FET mobilities on the spin-casting solvent was reported earlier for P3HT films [9]. The authors attributed the observed variation of mobility values with different solvents to differences in the film formation process.

In the present study, FET mobility measurements are performed to directly measure the change of mobility as a function of morphology. Based on the FET characteristics of MDMO-PPV films spin-cast from different solvents, the influence of interchain polymer aggregation on the hole field-effect mobility will be discussed.

2. Experimental

FETs (see Fig. 1(a)) were assembled on highly doped p^+ Si-substrates, used as gate electrode. An insulating oxide (232 nm) was thermally grown on one side of the substrate, and the backside was covered with an Al layer as the gate connection. A structure of TiW/Au interdigitating fingers, forming the source and drain electrodes, was realized on top of the insulating SiO_2 layer with a combination of photolithography and a lift-off process. The following combinations of conduction channel width (W μm) and length (L μm) were produced: $W/L = 1075/10$, 1035/5 and 550/3. Finally, after cleaning the substrate, the organic semiconducting layer was spin-cast to fill the channel. Pristine MDMO-PPV (obtained from Covion) was

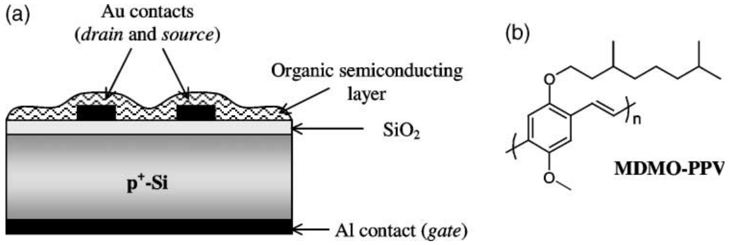

Fig. 1. (a) FET device structure and (b) chemical structure of MDMO-PPV.

deposited from 0.5% (5 mg/ml) toluene and CB solutions. The chemical structure of MDMO-PPV is shown in Fig. 1(b). For the studied p-channel operation, a negative gate voltage was applied to induce an accumulation layer of holes, allowing the measurement of the hole mobility. To facilitate the injection of holes into the highest occupied molecular orbital level of the channel material Au source and drain electrodes were used. The FET characteristics were measured using a HP4156A analyzer, with the source contact connected to ground. The measurements were performed with a long integration time (320 ms) to prevent capacitive charging effects of the transistor channel during sweeps of the drain-source voltage. Such capacitive effects were observed for short integration time (640 μs), leading to an overestimation of the mobility values [10]. All measurements were performed under a nitrogen gas flow.

The particle size (PS) distribution in the MDMO-PPV solutions was determined by means of light scattering measurements using a Microtrac Utrafine Particle Analyzer.

3. Results and discussion

Field-effect mobilities μ_{FE} were calculated from the saturation regime of the drain–source current (I_{ds}) using the formula [11]

$$I_{ds,sat} = \frac{\mu_{FE} W C_{ox}}{2L}\left(V_{gs} - V_t\right)^2, \qquad (1)$$

where W and L are the conduction channel width and length, respectively, C_{ox} is the capacitance of the insulating SiO_2 layer, V_{gs} is the gate voltage, and V_t is the threshold voltage. Eq. (1) is commonly used to estimate mobility values from organic FET characteristics and predicts that the squareroot of $I_{ds,sat}$ as a function of V_{gs} should give a straight line.

Fig. 2 shows the FET characteristics of a device in p-channel mode with MDMO-PPV as the channel material. Fig. 2(a) and (b) show the results obtained for MDMO-PPV spin-cast from a toluene solution. The hole current I_{ds} reaches saturation for negative applied V_{ds} and V_{gs} (Fig. 2(a)). The saturation point of $V_{ds} = -90$ V was used to plot the V_{gs} dependence in Fig. 2(b). From the slope of the linear fit at high negative V_{gs}, a field-effect hole mobility of $\mu_{FE} = 5 \times 10^{-6}$ cm^2/V s was calculated using Eq. (1). The same procedure was followed to derive the FET parameters of MDMO-PPV that was deposited from a CB solution (Fig. 2(c) and (d)). A hole mobility of 3×10^{-5} cm^2/V s was obtained. The use of CB as solvent clearly enhances the hole mobility of MDMO-PPV as compared to toluene. We attribute the increase in mobility in the CB-cast film to a modification of the polymer morphology. Previous results by Nguyen et al. [12] demonstrated that organic light-emitting diodes based on MEH-PPV, a conjugated polymer very similar in structure to MDMO-PPV, exhibit a higher current for films spin-cast from a CB solution as compared to other common solvents. This was explained by assuming that an increased intermolecular coupling of a larger number of chromophore aggregates takes place [4], leading to higher charge carrier mobility. In another paper, Nguyen et al. [13] concluded, based on light scattering experiments, that the aggregation of MEH-PPV is promoted in CB because of the more open conformation that the polymer chains adopt in CB, as compared to THF.

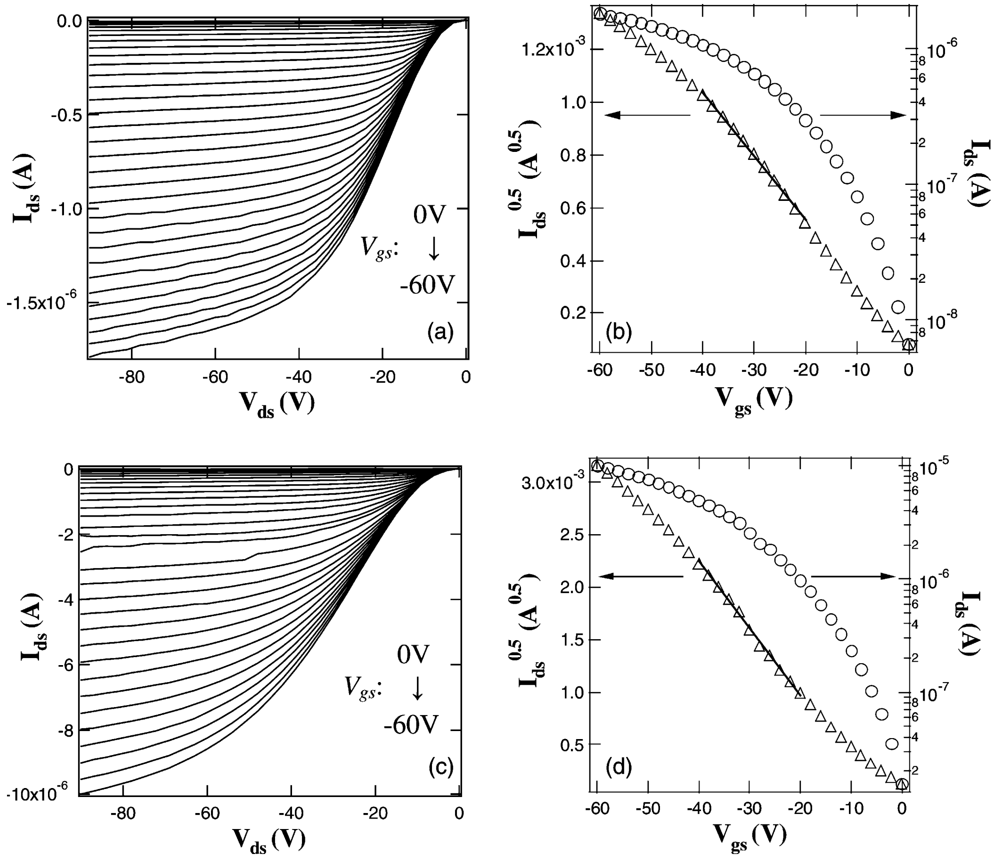

Fig. 2. (a) I_{ds} versus V_{ds} characteristics of an MDMO-PPV FET cast from toluene solution, with Au contacts and a source to drain gap of $L = 3$ μm. (b) I_{ds} plotted as a function of V_{gs} for $V_{ds} = -90$ V on a logarithmic scale (right axis, circles). $I_{ds}^{1/2}$ plotted as a function of V_{gs} (left axis, triangles). From the slope at high negative V_{gs}, the field-effect mobility of toluene-based MDMO-PPV for holes is calculated to be $\mu_{FE} = 5 \times 10^{-6}$ cm^2/V s. (c) Idem for MDMO-PPV cast from CB. (d) Idem for CB-based MDMO-PPV yielding $\mu_{FE} = 3 \times 10^{-5}$ cm^2/V s.

We used light scattering to compare the aggregation of solutions of MDMO-PPV in toluene with that in CB. This technique allows to determine the PS in solutions, which can be expressed as a number distribution. Alternatively, the PS can also be represented as a volume distribution, giving the percentage of the total volume occupied by the particles with a certain size. The results for MDMO-PPV, dissolved in toluene and CB with different concentrations (0.0625%, 0.125% and 0.25%), are given in Table 1. The PS that are shown in Table 1 mean that 90% of the number (or volume) of particles is below the given value. The rows "volume/fraction average" indicate the average PS in several (if present) distinct fractions of the volume distribution. It can be seen from Table 1 that in toluene, the number PS develops upon dilution from 35 nm over 6 nm to more than 6 μm. The volume PS increases from 2.2 μm over 3.2 μm to >6 μm. At the highest concentration (0.25%), 2 fractions can be distinguished from which the smaller decreases further in the first dilution and completely vanishes at the lowest concentration (0.0625%). The latter is indicative for a true solution. At the concentration of 0.25%, toluene provides at least a partial solubility for MDMO-PPV. In this case, vacancies are created within the polymer coil that can be occupied by toluene molecules, that in this way possibly hinder interchain interactions. In CB, the number PS decreases from

Table 1
Overview of the light scattering measurements on toluene and CB solutions of MDMO-PPV

		Particle size (nm) as a function of concentration[a]		
		0.25%	0.125%	0.0625%
Toluene	Number distribution	35	6	6240
	Volume distribution	2265	3240	>6000
	Volume/fraction average	30; 1050	6; 1000–3000	>6000
CB	Number distribution	66	8	8
	Volume distribution	1565	8	5585
	Volume/fraction average	40; 70; 120; 1200	8	8; 5500

The PSs are shown for different concentrations. More details are given in the text.

[a] 90% of the number or of the volume are below the given value.

66 down to 8 nm upon dilution. The volume PS first decreases from 1565 to 8 nm, then rises again to 5585 nm. At the concentration of 0.25%, there are four (partially overlapping) PS fractions, which are reduced to just one fraction at medium concentration. At the lowest concentration, a new fraction develops around a PS of 5.5 μm. These data indicate that the CB solutions with high and medium concentrations form a colloidal system, rather than a solution. It is likely to assume that in these colloids chromophore aggregation and thus interchain interactions are promoted. Nevertheless, one should note that these measurements did not give evidence of any change of polymer chain conformation.

As the degree of aggregation is known to be preserved throughout the spin-casting process [13], we can conclude that the results of the light scattering experiments on the MDMO-PPV solutions support the mobility results of the MDMO-PPV films: the higher degree of interchain aggregation of the films spin-cast from CB, as compared to those spin-cast from toluene, can explain the higher mobility value measured in the CB-cast films.

4. Conclusions

In conclusion, the field-effect hole mobilities of pristine MDMO-PPV, spin-cast from toluene and CB solutions, have been measured to be $\mu_{FE} = 5 \times 10^{-6}$ and 3×10^{-5} cm^2/V s, respectively. This difference is attributed to the different degree of interchain aggregation introduced by a solvent induced modification of the polymer morphology. A solvent-dependent increase of mobility is also reflected in recent results concerning the performance of photovoltaic cells based on organic blends of MDMO-PPV and [6,6]PCBM that were spin-cast from toluene and CB solutions [14].

Acknowledgements

Financial support from the Austrian FWF (Lise Meitner Stipendium, project no. M539-CHE for S. E. S.), the Magistrat Linz and the IWT (Flemish Institute for Promotion of Scientific Technological Research in the Industry for W.G.) is gratefully acknowledged.

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