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Performance spread reduction in organic field-effect transistors using semiconducting liquid-crystal polymers

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We report on a semiconducting liquid-crystal polymer (LCP) for organic field-effect transistors (OFET) showing comparable charge carrier mobilities to 6,13-bis(triisopropylsilyl)ethynylpentacene (TIPS-PEN) on same test structures using organic dielectrics. In addition, we demonstrate a spread reduction of the OFET parameters by using the LCP allowing the fabrication of transistor devices in a simple processing procedure with a high reproducibility compared to TIPS-PEN, which is essential for the functionality of organic integrated circuits. Investigations of the molecular structure of the LCP reveal a high ordering of the molecules even in the liquid phase which further improves after annealing. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4820144>]

In recent years large effort has been made in the investigation of organic field-effect transistors (OFET) and integrated circuits using 6,13-bis(triisopropylsilyl)ethynylpentacene (TIPS-PEN) as the semiconductor for solution-based processes, paving the way for low-cost and large-area technologies.^{1–4} Mobilities of 1.5 cm²/Vs and beyond have been reported for this material, due to its ability to form large crystals with a very high molecular order.⁵ In contrast to the face-to-edge herringbone structure observed in unmodified pentacene, the bulky side groups of TIPS-PEN cause the molecule to primarily pack in a face-to-face structure, leading to an improved π -orbital overlap.⁶ One major drawback of this material is the difficulty in controlling homogenous crystal growth over a large area. This is a crucial aspect because the crystal size and orientation of the organic semiconductor have a significant impact on the performance of the transistor.^{7,8} Inhomogeneous crystal growth of the semiconducting layer can lead to large variations in the transistor performances, thus, in turn, affecting the function of integrated circuits. Therefore it is highly desirable to have a homogenous crystal growth of the organic semiconductor, especially for large areas, e.g., in roll-to-roll fabrication. The molecular ordering of TIPS-PEN has been shown to be strongly dependent on the solvent and the drying environment.^{9–11} Several approaches have been investigated to overcome this issue of a homogenous crystallization process, e.g., by selective surface energy modifications,¹² using two-liquid systems,¹³ solution-shearing techniques,¹⁴ co-solvent systems,^{10,15} or blending with other polymers.^{16,17}

In this work we demonstrate another approach to fabricate high performance transistor devices over a large area with good reproducibility by using a semiconducting liquid-crystal polymer (LCP). Organic field-effect transistors based on TIPS-PEN and LCP are fabricated under similar conditions and compared with regards to their electrical

characteristics and the spread in performance from device to device. The charge carrier mobility of conjugated polymers has been steadily improving over recent years due to a combination of new materials design, optimized device architectures, and improvements in thin film processing, with charge carrier mobilities for p-type polymers in excess of 2 cm²/Vs now being reported. A common design feature of these high performance polymers is a conjugated backbone consisting of co-polymerized donor and acceptor motifs. The hybridization of the resulting molecular orbitals leads to low band gaps and often a rigidification of the polymer backbone. This has been shown to lead to close intermolecular contacts. In addition, through the use of appropriate alkyl side-chains, liquid crystalline like phase behavior can be induced either directly in the polymer itself (thermotropic phases) or in mixtures of polymer/solvent (lyotropic phases), which occur during processing. Indeed, many of these high performing polymers are noted to aggregate strongly in solution, a feature which may result in lyotropic phases and ordering during processing. Here we report the investigation of a proprietary donor-acceptor co-polymer (FS090) which demonstrates a strong tendency to self-order upon thin film formation. This liquid crystalline like behavior is shown to result in a significant enhancement in device to device reproducibility.

For the material evaluation a bottom-gate configuration was chosen because of the convenient and easy processing of the gate electrodes via photolithography. To avoid any influence on the morphology of the organic semiconductor due to the source and drain electrodes and to minimize contact resistance issues, a top-contact configuration was preferred. The device architecture is presented in Fig. 1. OFETs were fabricated on cleaned 6 in.-borosilicate glass wafers. The gate electrode was formed by sputtering a 100 nm thick aluminum layer on the wafers and structuring via photolithography. Poly(4-vinylphenol) (PVP) (Sigma-Aldrich, Mw ~ 25 000) was dissolved in n-butanol, and polymelamine(co-formaldehyde) was added as the crosslinking agent. The solution was

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FIG. 1. Device architecture of the OFET test structures.

filtered through a 0.44 μm syringe-filter and spin-coated at 1500 rpm for 30 s onto the substrates. The PVP dielectric film was baked for 5 min at 100 $^{\circ}\text{C}$ and finally cross-linked at 200 $^{\circ}\text{C}$ for 20 min, resulting in film thicknesses of 1.3 μm .

TIPS-PEN was dissolved in p-xylene at a concentration of 18 mg/ml and poly(α -methylstyrene) (Sigma-Aldrich, Mw $\sim$ 437 000) was added as a blending material at a ratio of 2:2:96. The solution was filtered through a 0.2 μm syringe-filter, spin-coated onto the PVP-coated glass wafers, and the substrates were immediately put into a crystallization chamber for 15 min to facilitate a very slow solvent evaporation, enhancing a large crystal growth of the TIPS-PEN. To remove residual solvent the substrates were finally baked on a hotplate at 120 $^{\circ}\text{C}$ for 20 min. The LCP FS090 was dissolved in 1,2-dichlorobenzene at a concentration ratio of 10 mg/ml and filtered through a 0.2 μm syringe-filter. The solution was spin-coated at 2000 rpm for 20 s onto the glass substrates followed by a drying step of the films on a hotplate at 100 $^{\circ}\text{C}$ for 5 min. FS090 is a low band gap LCP consisting of a donor-acceptor type structure. It has a number average molecular mass (Mn) of 32 000 g/mol and a polydispersity of 2.9 as measured by gel permeation in chlorobenzene at 80 $^{\circ}\text{C}$ against polystyrene standards. After the deposition of the

TABLE I. Extracted parameters for TIPS-PEN and FS090.

	TIPS-PEN	FS090
Field-effect mobility μ_{sat}	$0.13 \text{ cm}^2/\text{Vs} \pm 0.1 \text{ cm}^2/\text{Vs}$	$0.1 \text{ cm}^2/\text{Vs} \pm 0.02 \text{ cm}^2/\text{Vs}$
Threshold voltage V_{TH}	$0.7 \text{ V} \pm 1.5 \text{ V}$	$-1.8 \text{ V} \pm 0.7 \text{ V}$
On/off-ratio	2×10^3	7×10^2

organic semiconductor, gold top electrodes were formed by evaporation through a shadowmask resulting in thicknesses of about 100 nm.

The transistors used in this comparative study have channel widths of 3.5 mm and channel lengths of 100, 150, 250, and 300 μm . For the characterization, three test wafers for TIPS-PEN and FS090 were fabricated, and a minimum of five transistors of all channel lengths were measured for each of the samples using a Keithley 4200 semiconductor parameter analyzer. Representative transfer [i.e., drain current (I_{D}) versus gate voltage (V_{G}) at a fixed drain voltage (V_{D}) of -40 V] and output curves [i.e., I_{D} versus V_{D} measured at different V_{G}] for the TIPS-PEN and FS090 transistors are given in Fig. 2.

We highlight that all fabrication and characterization steps were carried out in ambient atmosphere and normal laboratory environment except for the photolithography patterning of the gate electrodes, which were performed in a cleanroom. Measurement was carried out directly after fabrication. The field-effect mobility μ_{sat} was calculated in the saturation regime from the linear fit of $(I_{\text{D}})^{1/2}$ versus V_{G} , and threshold voltage V_{TH} was extrapolated from the intercept point of the linear fit and the V_{G} -axis. The mean values for field-effect mobility μ_{sat} , threshold voltage V_{TH} , and $I_{\text{On}}/I_{\text{Off}}$ ratio for both materials are listed in Table I.

FIG. 2. Representative transfer and output curves for (a), (b) TIPS-PEN, and (c), (d) FS090 transistors with channel width and length of 3.5 mm and 100 μm , respectively.

FIG. 3. Set of 15 transfer curves taken from three test wafers for (a) TIPS-PEN and (b) FS090 at gate length of $300\ \mu\text{m}$.

FIG. 4. Histogram of the distribution of (a) field-effect mobility and (b) threshold voltage for a total number of 60 transistor devices with varying channel lengths of 100, 150, 250, and $300\ \mu\text{m}$ for TIPS-PEN and FS090, respectively.

From the characteristics and the transistor parameters it can be seen that the mean performance of the TIPS-PEN transistors is slightly higher than that of the LCP. However, two major drawbacks of TIPS-PEN have to be taken into account. In comparison with the transfer curve of the LCP in Fig. 2(c), the TIPS-PEN characteristic in Fig. 2(a) shows a larger hysteresis, which we attribute to a larger trap density at the semiconductor/dielectric interface. Also, the spread in transistor performance is much higher than that of FS090. TIPS-PEN transistors showed mobilities ranging from 0.02 to $0.4\ \text{cm}^2/\text{Vs}$ measured on all three test wafers whereas the FS090 transistors had mobilities from 0.07 to $0.16\ \text{cm}^2/\text{Vs}$. In addition, variations in the threshold voltage are also reduced by the use of LCP material. The low on/off current ratio for both materials is attributed to the fact that the active layer pattern is not precisely defined in spin coated devices which leads to a high leakage current flow through the active layer in the off-state. Higher mobilities and better on/off ratios have previously been demonstrated for these materials; however, in these instances significantly more complex processing procedures were required. In our case, we wished to maintain a simple processing procedure, which did not use any additional processing to isolate the transistors and improve the on/off ratio since we were interested to investigate the intrinsic parameter spread in these two classes of materials. Fig. 3 shows a set of 15 transfer curves of all three test wafers for both materials at gate length of $300\ \mu\text{m}$ emphasizing the impact of the deviation in transistor performances.

From the curves in Fig. 3 it can be seen that the spread is strongly reduced by using the LCP material. Similar results were obtained with channel lengths of 100, 150, and $250\ \mu\text{m}$. In order to summarize the spread in performance in a graphical representation, the field-effect mobilities and threshold voltages of all measured transistor devices for

TIPS-PEN and FS090 are plotted in a histogram as seen in Fig. 4. To improve the statistical confidence level, 15 devices for each channel length were taken into account, yielding a total number of 60 measured transistors for TIPS-PEN and FS090, respectively. From Fig. 4(a) it can be seen that the distribution of the field-effect mobility for FS090 is by far lower than that of TIPS-PEN. A similar observation can be made with the threshold voltage in Fig. 4(b) although here the reduction of the distribution is not so intensive as compared to the field-effect mobility. We believe the reduction in the spread of performance may be related to the differences in crystallite size and orientation between the small molecule and the LCP. In order to verify this assumption, films of FS090 were investigated by grazing incidence x-ray diffraction (GIXRD), both as cast and after annealing at 100°C for 10 min. As can be seen in Fig. 5, the as-cast films already show clear signs of ordering, with a clear diffraction peak at

FIG. 5. GIXRD spectra of FS090 as-cast and after annealing at 100°C for 5 min.

$2\theta = 4.5^\circ$, corresponding to a distance of $19.6 \text{ \AA}$ which we attribute to the lamellar packing distance between the conjugated polymer backbones. After annealing the ordering of the film clearly improves, the main diffraction peak at 4.5° increases in intensity, and second, third, and fourth order reflection become visible at 9° , 13.5° , and 18° , respectively. This increase in order upon annealing clearly correlates to the improved transistor performance observed.

In conclusion, we have demonstrated a way to reduce the transistor performance spread of commonly used organic semiconductors due to inhomogeneous crystal growth by using a liquid-crystal polymer as the semiconductor. This material enables good device to device reproducibility over large area arrays with similar device characteristics in performance.

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