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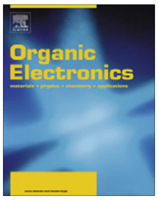

Polymer blended small molecule organic field effect transistors with improved device-to-device uniformity and operational stability

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ABSTRACT

We report high performance organic thin-film transistors (OTFTs) with improved device-to-device uniformity and operational stability using polymer-blended small molecule organic semiconductor, 2,8-difluoro-5,11-bis(triethylsilylethynyl) anthradithiophene (diF-TESADT). The diF-TESADT blended with poly(α-methylstyrene) was spin-cast to form bottom-contact OTFTs, and an average carrier mobility of more than 0.16 $cm^2/V\,s$ with more uniform surface morphology and device-to-device uniformity compared to neat diF-TESADT devices were achieved. Additionally, the polymer-blended OTFTs have shown improved operational stability under gate bias-stress possibly due to blocking of ambient oxygen and moisture by vertically separated insulating matrix polymer.

1. Introduction

Key requirements for successful approaches of organic electronics include low cost processing, high performance devices with good device-to-device uniformity, and their operational and environmental stability. Solution-processed organic thin-film transistors (OTFTs) are of particular interest due to their potential for use in low-cost manufacturing techniques such as printing and roll-to-roll processing [1–3]. Recently, lots of high performance solution processible small molecules as well as advancements in device fabrication have been demonstrated [4–7], and the development of advanced technologies for achieving high uniformity and stability of the organic devices are now being addressed. For example, high mobility solution-processed small molecular OTFTs were recently reported using acene-based derivatives [5]. These spin-cast OTFTs had field effect mobility higher than 3 $cm^2/V\,s$ using bottom-gate and bottom-contact structures [5]. Although the small molecule materials have shown high mobility but also have indicated large variation of device performance possibly due to non-uniformity of the semiconductor layer, which is caused by the difficulties of controlling semiconductor morphology and crystallinity.

Recently, polymer/small molecule blending system for high-mobility solution-deposited organic electronics is of great interest. By blending semiconducting or insulating polymer with small molecule semiconductors, improvement in electrical properties has been reported [8–10]. In addition to the improvement in the electrical properties, influence of polymer blending on device-to-device uniformity and operational stability should be also considered especially in case of using small-molecule organic semiconductors such as 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-pentacene) and 2,8-difluoro-5,11-bis(triethylsilylethynyl) anthradithiophene (diF-TESADT). Typically, these solution processed small-molecule organic semiconductors have polycrystalline structure and as a result rather wide distribution of field-effect mobility is observed due to difference in the degree of crystallization and mobility anisotropy with crystal orientation [11]. Therefore, for a possible application of small-molecule based organic transistors in large-area electronics, it is

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important to achieve higher performance uniformity with a narrow distribution.

In this report, a blending system of polymer insulating material and high performance small molecule organic semiconductor was used as a channel layer and it was found that the polymer blending affects the device-to-device uniformity and as well as the operational stability of the device. By optimizing the mixing ratio between the blending polymer and small molecule semiconductor, improved device-to-device uniformity and operational stability have been realized.

2. Experimental details

Simple bottom-gate and bottom-contact TFT structure has been used to evaluate the transistor characteristics. A 200 nm-thick layer of silicon dioxide was thermally grown as a gate dielectric on heavily doped (0.05 Ω cm) n-type silicon wafers. The doped silicon wafer was used as both the sample substrate and gate electrode. One hundred nanometer-thick Au source and drain electrodes were deposited by thermal evaporation and patterned using lift-off process. Prior to active layer deposition, the substrates were cleaned using UV/ozone treatment. A self-assembled monolayer of pentafluorobenzenethiol (PFBT, Aldrich) was formed on the Au source/drain electrodes to modify organic semiconductor microstructure and to improve the metal/organic contact and device performance [12]. Also, the surface of SiO_2 gate dielectric layer was modified with hexamethyldisilazane (HMDS, Aldrich) by using solution-process. The detailed surface treatment processes were reported in our previous paper [12]. After modification of the surfaces, an active layer was spun over the pre-patterned source/drain electrodes. Two types of semiconductor solutions were prepared; (1) neat diF-TESADT dissolved in chlorobenzene (2 wt.%), and (2) poly(α-methylstyrene) (PαMS, $M \approx 110{,}000$ g/mol, Aldrich) blended diF-TESADT in chlorobenzene with w/w ratio of 2:2. All solution preparation, device processing, and electrical measurements were performed in an air ambient.

3. Results and discussion

3.1. Film morphology

Polycrystalline organic semiconductors generally cause device uniformity problem due to uncontrollable grain growth, randomness in grain orientation and grain boundary effect, and it has been one of the factors limiting the scalability and mass production of organic electronics. Therefore, obtaining highly uniform organic semiconductor films from cost-effective solution-processing with acceptable electrical performance is one of the key challenges for commercializing large-scale organic electronics. Most of the high-performance small molecule organic semiconductors such as diF-TESADT and TIPS-pentacene, however, have polycrystalline structures when they are formed from solution-processing. As a result, non-uniform film morphology and rather poor device-to-device uniformity were typically observed. In Fig. 1(a), optical and laser confocal microscope images of spin-cast neat diF-TESADT films which were coated on PFBT-treated Au source/drain electrodes (with channel lengths of 5, 10, and 20 μm) are shown. Due to the PFBT treatment on Au electrodes, large-sized grains of diF-TESADT were formed at the channel region, and as shown in our previous reports, the diF-TESADT grains grew from the two PFBT-treated Au contacts and extend across (in shorter channel, <5 μm) or collided in the channel area resulting in a boundary-like structures (in longer channels, >10 μm). However, in all cases, non-uniform film morphologies were observed along with dewetting problem in some regions. On the other hand, PαMS-blended diF-TESADT films showed more improved film uniformity even in narrow regions between the source and drain electrodes as shown in Fig. 1(b). Comparison of atomic force microscopy images of both neat and PαMS-blended films (Fig. 2) also indicates that the polymer blending facilitates more smooth and controlled formation of organic semiconductor layers.

3.2. Electrical properties and device-to-device uniformity

Spin-cast neat diF-TESADT TFTs with PFBT-treated Au source/drain electrodes showed field-effect mobility of 0.1–0.5 $cm^2/V\,s$ with threshold voltage (V_{TH}) of 0–20 V, on/off ratio of $\sim 10^7$, and subthreshold slope of 0.3–1.5 V/dec. The averaged mobility was 0.24 $cm^2/V\,s$ with a standard deviation of 0.13 $cm^2/V\,s$. Fig. 3(a) and (b) shows typical output and transfer characteristics of a neat diF-TESADT TFT with channel length of 10 μm and channel width of 50 μm. Several kinds of devices with different blending ratio were tested and they have shown the expected electrical performance such as slightly lower mobility from the blending solution with higher PαMS addition. The PαMS blending slightly decreased the mobility as shown in Table 1. Averaged mobility was decreased to 0.16 $cm^2/V\,s$, and the output and transfer characteristics of blended TFTs are shown in Fig. 3(c) and (d). The mobility decrease in blended devices can be attributed to mainly two reasons; firstly, intrusion of insulating polymer chains, and secondly, deterioration in crystallinity due to blending polymer. During the film formation process, vertical phase separation of PαMS chains and diF-TESADT molecules is likely to occur. However, some of the insulating PαMS chains can remain in diF-TESADT-rich regions near the channel/gate dielectric interface affecting the carrier charge transport. Also, the PαMS chains may interrupt the growth of diF-TESADT crystals and change its crystal structure. Fig. 4 shows X-ray diffraction (XRD, θ–2θ mode) results for around 200 nm-thick neat diF-TESADT and PαMS-blended diF-TESADT films spin-cast on PFBT-treated Au layer. Single crystal diF-TESADT has a triclinic structure with unit cell parameters $a = 7.1153$ Å, $b = 7.2342$ Å, $c = 16.626$ Å, $\alpha = 97.522°$, $\beta = 91.361°$, and $\gamma = 107.491°$ [6]. From these parameters peaks observed at 5.4° (001), 17° (003), and 23.2° (004) indicate a well-ordered molecular structure with a vertical intermolecular spacing of 16.5 Å (*d*-spacing). Although the XRD data show good molecular ordering in both neat and PαMS-blended films, the polymer blended films indicates a little degradation

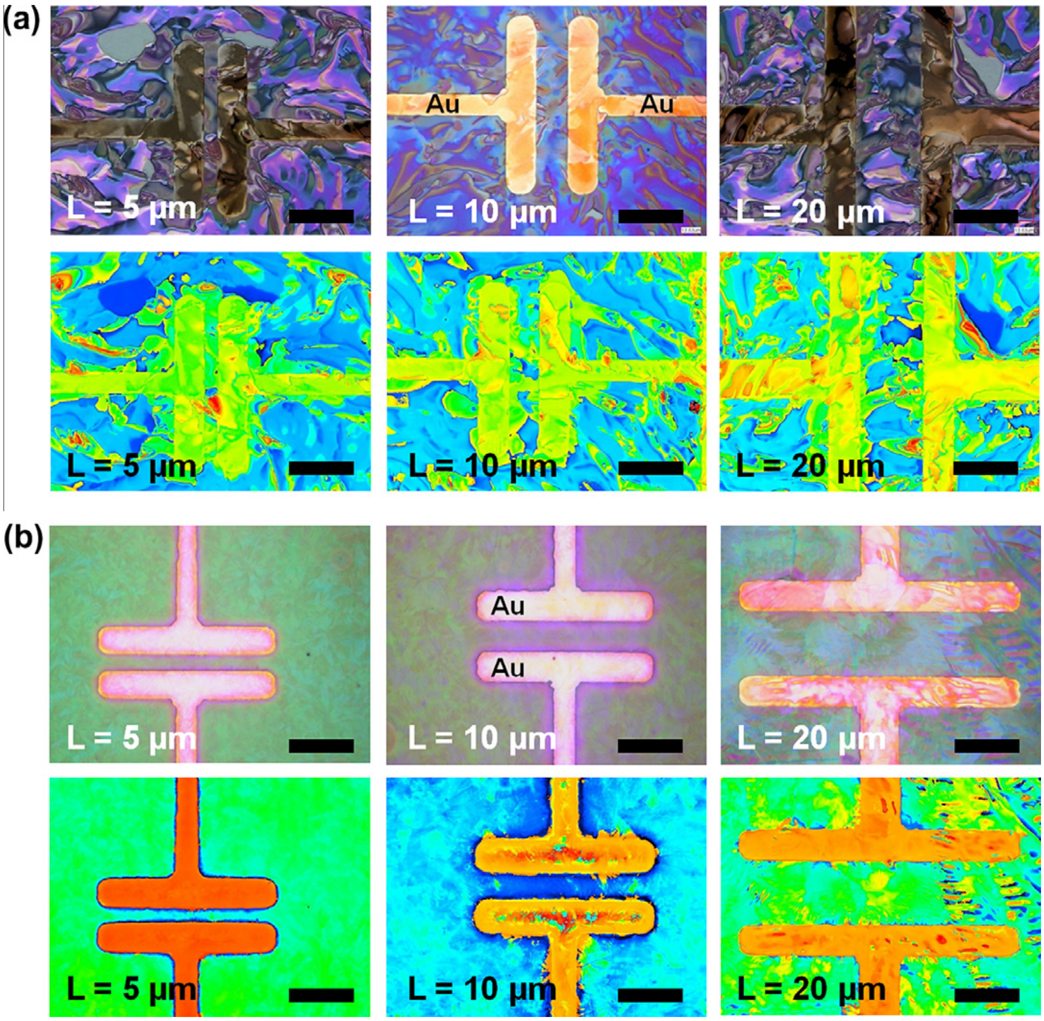

Fig. 1. Optical and laser confocal microscope images of spin-cast films from (a) neat diF-TESADT solution (2 wt.%) and (b) diF-TESADT/PαMS blend solution (2:2 w/w ratio). The laser confocal microscope images provide height variation in the samples. The scale bars indicate 20 μm.

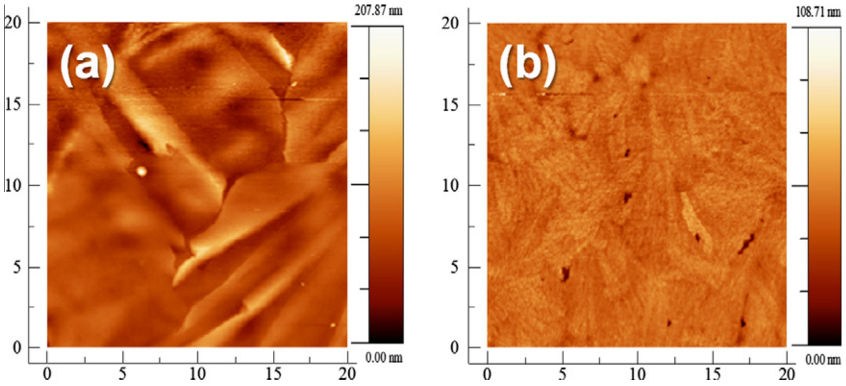

Fig. 2. Atomic force microscope images of spin-cast films from (a) neat diF-TESADT solution (2 wt.%) and (b) diF-TESADT/PαMS blend solution (2:2 w/w ratio) (scan size of 20 μm × 20 μm).

in the molecular ordering or crystalline structure. A small reduction in the peak intensity (inset of Fig. 4) reflects more disordered crystalline structure by PαMS blending and broadening of full width at half maximum (FWHM)

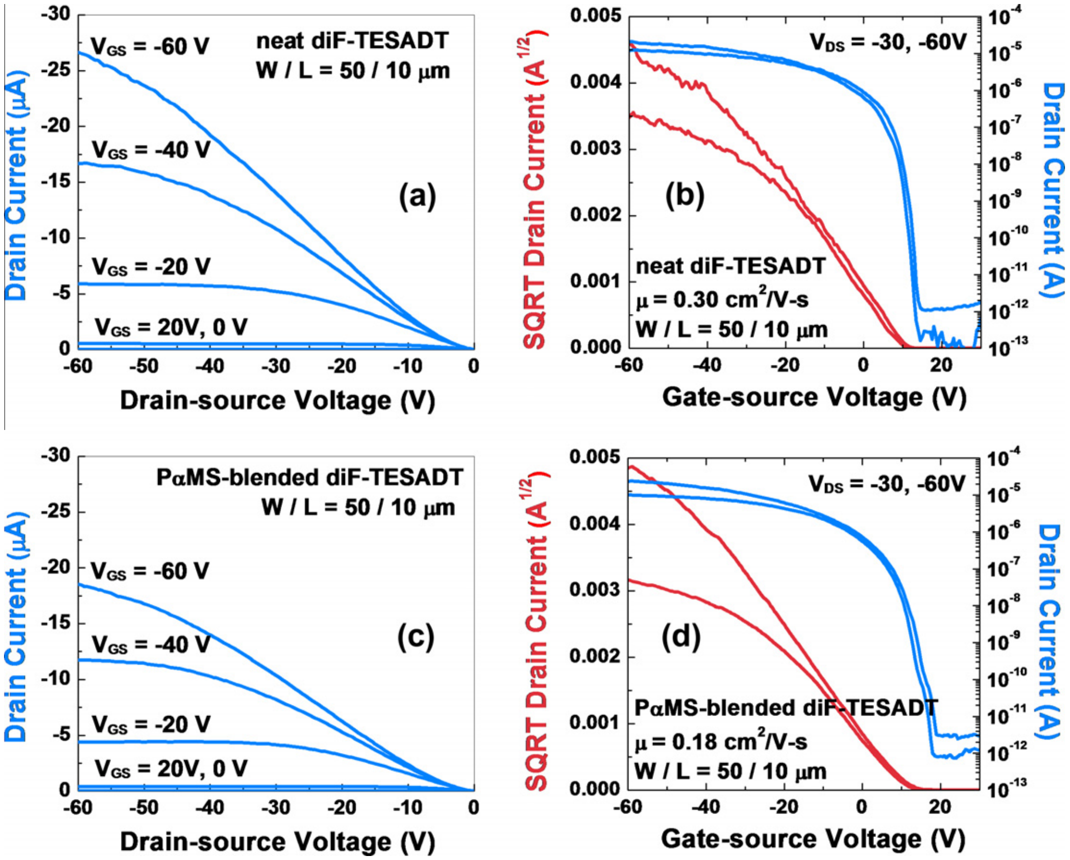

Fig. 3. Output and transfer characteristics of (a) and (b) neat diF-TESADT TFTs and (c) and (d) PαMS-blended diF-TESADT TFTs (2:2 w/w ratio) fabricated using PFBT-treated Au source/drain electrodes. The channel length and width of the devices were 10 μm and 50 μm, respectively.

Table 1
Electrical properties of spin-cast neat and PαMS-blended diF-TESADT TFTs using PFBT-treated Au electrodes. The electrical properties were obtained from devices with channel length and width of 10 μm and 50 μm, respectively.

Semiconductor layer (spin-cast)	Mobility (cm^2/V s)		Subthreshold slope (V/dec)	VTH (*V*)	On/off ratio
	Mean	Deviation			
Neat diF-TESADT	0.234	0.13	0.66	11.1	1.4×10^7
PαMS-blended diF-TESADT	0.16	0.05	1.15	9.9	4.3×10^6

from 0.320° to 0.333° shows reduction in the size of diF-TESADT crystallines. From these results, it is likely that the slight degradation in TFT performance of PαMS-blended devices is partially due to intrusion of insulating PαMS chains in the diF-TESADT-rich regions as well as somewhat deterioration in crystal quality of the semiconductor layer.

As can be expected from the improved film morphology by PαMS blending, the device-to-device uniformity of PαMS-blended TFTs has been greatly improved. Fig. 5 compares the distribution of field-effect mobilities of neat and PαMS-blended TFTs obtained from 30 to 50 devices for each set. As aforementioned, the average mobility of neat devices is higher than PαMS-blended devices. However, the blended devices had much narrower distribution of mobility with a standard deviation of 0.05 cm^2/V s indicating good device-to-device uniformity. The improved device-to-device uniformity may be attributed to the enhanced film uniformity from vertical separation of two components. Without blending polymer, large morphological anisotropy is expected due to strong interaction between diF-TESADT molecules rather than interaction with the substrate. As a result, non-uniform film morphology and rough surface is obtained as shown in Fig. 2(a). In contrast, with blending polymer, laterally homogeneous channel morphology is obtained as an effect of vertical separation of two components during the film formation process [9,13]. In vertical direction, normal to the channel surface, the composition ratio of the two components changes drastically due to vertical phase separation. However, in the in-plane direction, parallel to the channel surface, the composition ratio variation is small because the phase separation occurs preferentially only in the normal direction. Therefore, more laterally homogenous films can

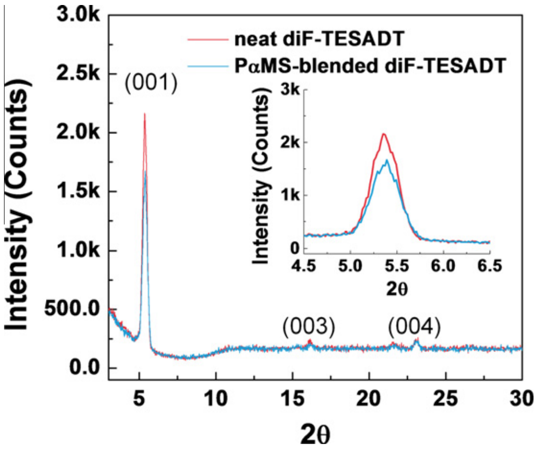

Fig. 4. Out-of-plane mode X-ray diffraction results of spin-cast neat and PαMS-blended diF-TESADT (2:2 w/w ratio) films on PFBT-treated Au layer. The inset image shows narrow region of $2\theta = 4.5–6.5°$ for (001) peaks.

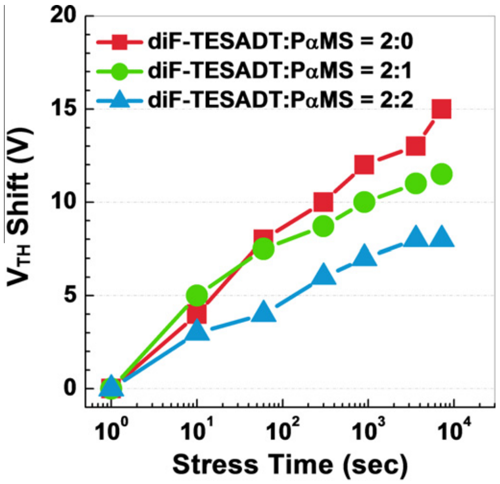

Fig. 6. Threshold voltage shift under gate-bias stress in neat and PMS-blended diF-TESADT TFTs (w/w ratio of 2:1 and 2:2). The gate-bias stress conditions were V_{GS} of −20 V, V_{DS} of −0.1 V, and bias stress time of 7200 s.

be obtained from the polymer-blended solution and provide devices with good device-to-device uniformity.

3.3. Operational stability

As an additional effect to the uniform film morphology by polymer blending, improved operational stability is expected due to in situ encapsulation of the active layer by the blending polymer [14,15]. Fig. 6 compares threshold voltage shift under gate-bias stress in both neat and PαMS-blended diF-TESADT TFTs (2:1 and 2:2 in w/w ratio). The gate-bias stress conditions were $V_{GS} = -20$ V, $V_{DS} = -0.1$ V, and bias stress time of 7200 s. As noted above, the polymer blended systems typically have shown multi-component semiconducting layer which was encapsulated in situ by the insulating polymer layer. Hamilton et al. reported that the vertical phase separation occurs in diF-TESADT/poly(triarylamine) (PTAA) and TIPS-pentacene/PTAA systems which was confirmed by dynamic secondary ion mass spectrometry [9]. Lee et al. and Kang et al. also have investigated the variation in the composition of TESADT/PMMA and TIPS-pentacene/PαMS films with depth by using photoelectron spectroscopy combined with argon sputtering system and neutron reflectometer, respectively [16,17]. In our previous experiments, it has been found that the ambient oxygen and moistures might penetrate into the grain boundaries and crystal structures, resulting in degradation of environmental and operational stability of the organic semiconductors [18]. Therefore, the encapsulated insulating polymer layer in the blended system may help to increase the operational stability of the device by blocking the oxygen and moistures penetrating into the grain boundaries and crystal structures of diF-TESADT.

In summary, blending insulating polymer such as PαMS with highly crystalline small molecule diF-TESADT may facilitate laterally homogenous film formation and good device-to-device uniformity. Additionally, improved operational stability which is possibly due to in situ formation of encapsulation layer by blending polymer was found. This work demonstrates that solution-processed polymer/

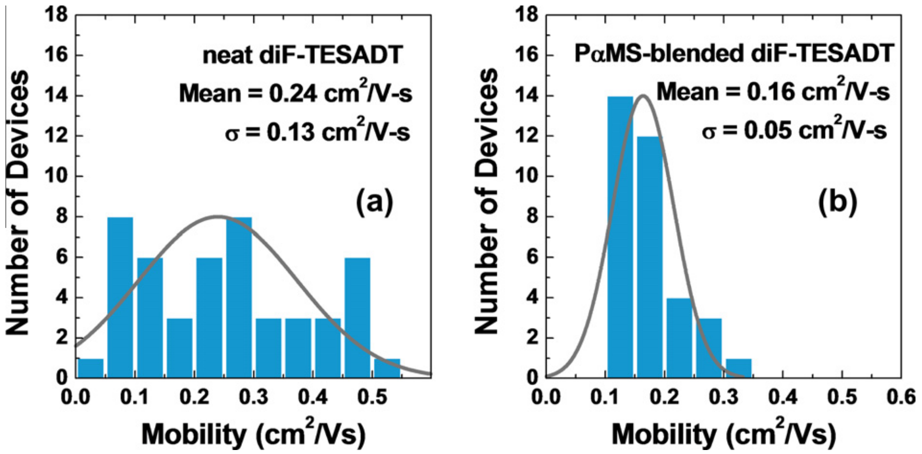

Fig. 5. Distribution of field-effect mobility obtained from (a) neat diF-TESADT TFTs (2 wt.%) and (b) PαMS-blended diF-TESADT TFTs (2:2 w/w ratio).

small molecule blended system can provide much improved device-to-device uniformity and operational stability also a possible path to low-cost and commercial compatible technology for large area organic electronics.

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