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Controllable electrical performance of spray-coated semiconducting small molecule/insulating polymer blend thin film for organic field effect transistors application

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ABSTRACT

A systematic study on solution content and solvent effect of spray-coated 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-PEN)/poly(α-methylstyrene) (PαMS) semiconducting blends for organic field effect transistors (OFETs) application was investigated based on different concentrations (10, 15 and 20 mg ml^{-1}), different compositions (TIPS-PEN/PαMS of 7/3, 5/5 and 3/7) and three different solvents, toluene (TOL), chlorobenzene (CB), and 1,2,3,4-tetrahydronaphthalene (THN). Polarized optical microscopy (POM), atomic force microscopy (AFM) and grazing-incidence X-ray diffraction (GIXRD) were used to evaluate the film morphology and chain orientation. The blend film can contribute to large coverage of TIPS-PEN carrier pathway across the OFETs channel if higher TIPS-PEN composition with suitable total blend concentration was introduced in the blend. Besides, the blend film processed from high boiling point THN can reduce the rate of evaporation which provides more time for TIPS-PEN migration to form a large grain of TIPS-PEN crystal. The resulting OFETs based on spray-coated from TIPS/PαMS (7/3) blend solution in THN exhibit maximum mobility of 3.23×10^{-1} cm^2 V^{-1} s^{-1} and ON/OFF ratio of >10^4.

1. Introduction

Organic field effect transistors (OFETs) comprising organic semiconductor as active channel have emerged as key element for realizing next generation of electronics [1–4]. To truly fulfill the low cost and large-area of electronic devices, organic semiconductor must be deposited from solution processes with more economical and versatile ways while still keeping high charge carrier mobilities. The casting procedure of organic semiconductor thin film from the solution which strongly changes the morphologies and crystalline alignment within semiconducting layer is the most important process to fabricate the OFETs. Although the vacuum-assisted deposition of small molecule semiconductors typically have demonstrated pretty high mobilities, the difficulties in fabricating uniform single crystals and depositing them in an appointed position are still challenging. However, the small molecule semiconductor solution is not viscous enough to be utilized as the liquid-substrate for the casting of such semiconductors, resulting in thin film dewetting. Also, the strong π-π interaction force between conjugated small molecules contributes to these localized/non-uniform crystalline morphologies. To break through these obstacles, the blend strategies, thus, potentially allows for achieving high mobilities of small molecule components combined with wetting agent for excellent thin film forming properties provided by polymers [5–8]. These blend films can be deposited from different solution techniques, and the final microstructures can be manipulated for higher electrical properties of OFETs [9].

Especially, system based on blending polymeric insulators with small molecules semiconductors has been investigated, such as blends of one of organic semiconductors, 6,13-bis (triisopropylsilylethynyl) pentacene (TIPS-PEN), 2,7-dioctyl[1]benzothieno[3,2-*b*][1]benzothiophene (C8-BTBT) and 2,8-difluoro-5,11-bis(triethylsilylethynyl)anthradithiophene (diF-TES-ADT), with one of the following insulating polymers, poly(methyl methacrylate) (PMMA), polystyrene (PS), poly(triarylamine) (PTAA) and poly(α-methylstyrene) (PαMS) [10–37]. The use of semiconducting small molecule/insulating polymer blend can contribute to simultaneous phase segregation between these two types of materials in the blend film with advantageous features of self-encapsulation for environmental stability [33], well-organized dielectric/semiconductor interface [11] and zone-refinement effect [15]. Solution process allows simple fabrication of polymer blended small molecular semiconductor film which can lead to enhanced and reproducible device performance through increased organization of the small molecules and uniform film

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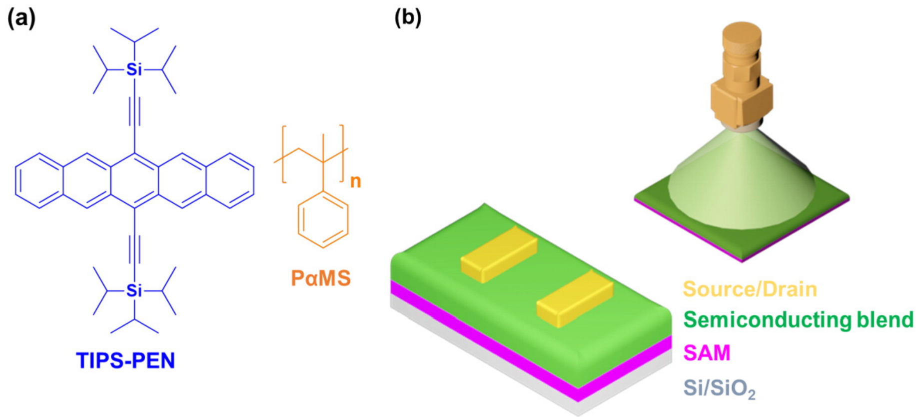

Fig. 1. (a) Chemical structures of semiconducting small molecules (TIPS-PEN) and insulating polymer matrix (PαMS). (b) Schematic illustration of spray-coated blend OFETs.

morphology mainly contributed from polymer. However, most of studies regarding to the solution processing of small molecules/polymer blend semiconductor film were mainly based on spin-casting [10–27] and inkjet printing [27–32] process. Spray-coating technique is considered as one of the most promising method for large scale and potentially low-cost manufacturing technique [38,39]. Since spray droplets are directly transferred from the nozzle to the substrate, this process can be done at high production speed and is compatible with all kinds of substrates. Although examples of spray deposition of organic semiconductors can be found in the previous report [36,40–43], spray-coating process of small molecule/polymer blend semiconductor solution and their blend film morphologies and corresponding electrical performance have not been systematically studied yet.

In this work, high mobility TIPS-PEN used as small molecule blending with environmentally stable PαMS insulating polymer was spray deposited onto the surface-modified dielectric/substrate for fabricating OFETs, as shown in Fig. 1. Specifically, blend solution concentrations, blend compositions between these two materials and solvents used for processing were compared with morphological and crystal packing characterized by polarized optical microscopy (POM), atomic force microscopy (AFM) and grazing-incidence X-ray diffraction (GIXRD) and charge transport in blend film performed by semiconductor analyzer. The relationship between the thin film microstructure, molecular orientation and electrical properties of OFETs can be established for our facile formation of crystalline semiconducting blends.

2. Experimental

2.1. Materials

6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-PEN) and poly(α-methylstyrene) (PαMS; M_w ~100,300, PDI ~1.05) were purchased from Luminescence Technology Corp. and Polymer Sources Inc., respectively. The solvents, such as toluene (TOL), chlorobenzene (CB), and 1,2,3,4-tetrahydronaphthalene (tetralin; THN), were purchased from Sigma-Aldrich of the anhydrous grade. Silane agent for the self-assembly monolayer (SAM) treatment, (2-phenylethyl)trichlorosilane (PETS), was supplied from Gelest, Inc. All the materials were used as-received without further purification.

2.2. OFETs fabrication and measurement

Discrete OFETs were fabricated on a heavily doped n-type Si wafer with a thermally-grown 300 nm-thick SiO_2 dielectric layer. The substrates were sequentially washed by sonication in toluene, acetone and isopropanol, and then cleaned with UV/ozone cleaner, prior to immersion in a solution of 5 mM PETS in toluene kept at 50 °C for 90 min. After that, the TIPS-PEN small molecule semiconductor and PαMS insulating polymer were combined in a weight ratio of 3/7, 5/5 and 7/3, and dissolved in the solvents of TOL, CB, THN at a concentration of 10, 15 and 20 mg ml^{-1}. The blend solution was sprayed with a pneumatic spray nozzle (Lumina LRK-AS8) at a solution flow rate of ~30 μl s^{-1} while clean compressed air at 0.1 MPa was used as carrier gas. The standoff distance between nozzle and substrate (1.2×1.2 cm^2) was 11–15 cm and the deposited substrates were kept at 30 °C and in ambient atmosphere. After solvent drying in air, the deposited semiconducting TIPS-PEN/PαMS blend thin film layer was annealed at 120 °C on a hot plate for 30 min in a N_2-filled glove box. Au top-contact source/drain electrodes (60–70 nm thickness) were deposited by thermal evaporation through a patterned metal shadow mask. The channel length (L) and width (W) were 25 and 1500 μm, respectively. Electrical characterization of OFETs was carried out in a N_2-filled glove box and recorded using a Keithley 4200-SCS semiconductor parameter analyzer.

2.3. Film structure analysis

TIPS-PEN/PαMS blend films were prepared for structural analysis on PETS-treated Si/SiO_2 substrates, in the same manner as for the OFETs fabrication process but without Au electrode on the top. Polarized optical micrographs were obtained by Leica 2700 M. UV–Vis spectrum was characterized by JASCO V-670 UV–Vis spectrophotometer. AFM of

Table 1
Summary of the electrical performance based on the TIPS-PEN/PαMS blend OFETs.

Total concentration (mg ml^{-1})	Solvent	TIPS-PEN/PαMS ratio (w/w)	Maximum mobility ($cm^2 V^{-1} s^{-1}$)	Average mobility ($cm^2 V^{-1} s^{-1}$)	Threshold voltage (V)	ON/OFF ratio
10	THN	5/5	8.62×10^{-5}	$5.32(\pm 3.14) \times 10^{-5}$	-23.4 ± 6.9	$1.4(\pm 1.8) \times 10^5$
15	THN	3/7	1.35×10^{-4}	$8.17(\pm 5.61) \times 10^{-5}$	-8.9 ± 2.8	$3.6(\pm 4.3) \times 10^5$
15	THN	5/5	4.76×10^{-2}	$3.04(\pm 1.50) \times 10^{-2}$	-27.1 ± 3.2	$1.5(\pm 2.1) \times 10^5$
15	THN	7/3	3.23×10^{-1}	$2.16(\pm 0.82) \times 10^{-1}$	-30.4 ± 7.7	$2.1(\pm 1.4) \times 10^4$
15	TOL	7/3	8.21×10^{-5}	$5.74(\pm 2.48) \times 10^{-5}$	-1.81 ± 1.1	$2.9(\pm 1.6) \times 10^3$
15	CB	7/3	1.87×10^{-3}	$1.58(\pm 0.26) \times 10^{-3}$	-6.84 ± 1.2	$1.9(\pm 0.7) \times 10^4$
20	THN	5/5	8.88×10^{-4}	$6.13(\pm 2.54) \times 10^{-4}$	-16.5 ± 5.9	$7.1(\pm 9.2) \times 10^4$

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