Organic Electronics 15 (2014) 3101–3110

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Modulation of surface solubility and wettability for high-performance inkjet-printed organic transistors

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A R T I C L E I N F O

Article history:
Received 26 June 2014
Received in revised form 25 August 2014
Accepted 30 August 2014
Available online 16 September 2014

Keywords:
Inkjet printing
Organic thin-film transistor
6,13-Bis(triisopropylsiylethynyl) pentacene
Dielectric interface
Solubility

A B S T R A C T

The surface solubility and wettability of photosensitive layers of polystyrene (PS) were engineered to evaluate its effect on the crystalline microstructure and film morphology of inkjet-printed 6,13-bis(triisopropylsiylethynyl) pentacene (TIPS-pentacene). UV exposure proved to be a simple and effective method for modulating the solubility of PS films with controllable crosslinking. As compared with the untreated PS film, the film morphology of the printed semiconductor on the UV-irradiated crosslinked PS films was significantly optimized. The optimal degree of crosslinking and solubility of the PS film were achieved by UV irradiation at a dose of 0.417 J cm^{-2}. Field-effect transistors fabricated using well-organized crystals on the optimal crosslinked PS film exhibited a maximum mobility of 0.48 $cm^2 V^{-1} s^{-1}$ and an average value of 0.19 $cm^2 V^{-1} s^{-1}$. The performance is clearly superior to that of devices prepared on a pristine PS film (0.02 $cm^2 V^{-1} s^{-1}$).

1. Introduction

Organic thin-film transistors (OTFTs) based on solution-processed organic semiconductors have attracted much research interest owing to their potential applications in low-cost large-area flexible electronics by the high-throughput printing process [1–10]. Among the established printing technologies, inkjet printing is very promising because the film of the printed material can be directly patterned without the use of a mask or additional etching processes [11–13]. The direct writing capability of inkjet printing allows for the deposition of various layers in OTFTs including the electrodes, semiconductor layer, and gate dielectric [14–18]. In particular, significant efforts have been devoted to the printing of organic semiconductors with controlled crystallographic morphology because charge carrier transport occurs in the semiconductor layer. The printing of organic semiconductor films with uniform morphology and desired mesoscale and nanoscale structures is a critical step for achieving high-performance devices [19]. In a typical inkjet printing process, ink droplets are propelled from a low-viscosity ink solution onto a surface. The composition of the ink, surface properties, and evaporation environment critically determine the exact position and morphology of the resulting semiconductor, as well as the electrical performance.

The soluble small-molecule organic semiconductor 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-pentacene) has been intensively investigated as the active layer for p-type OTFTs due to its good solubility in common

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http://dx.doi.org/10.1016/j.orgel.2014.08.059
1566-1199/

solvents and high-mobility field-effect charge transport [20–22]. A maximum hole mobility as high as 11 $cm^2 V^{-1} s^{-1}$ has been reported [23]. However, the inkjet printing of TIPS-pentacene films with high precision, uniform morphology, and desired crystalline microstructures is challenging because the strong intermolecular π–π interactions tend to induce thin-film dewetting and localized crystal anisotropy [24,25]. To overcome these limitations, the effects of the hydrodynamic flow in a drying droplet and the surface wettability of the dielectric substrate on the crystalline microstructures of the printed TIPS-pentacene, as well as film morphology, have been systematically studied [26–31]. Recently, an inkjet-printed TIPS-pentacene single crystal has been realized using local patterns on the substrate surface and a co-solvent system [32,33]. However, the pre-patterning processes rely on complicated and expensive photolithography techniques, which are possible obstacles to its applications.

Another promising method for improving the film-forming properties and film uniformity of solution-processed small organic semiconductors is to blend with insulating or semiconducting polymers. OTFTs based on spin-coated films of such blends have exhibited enhanced mobility and improved uniformity and thermal stability [34–38]. This concept has also been successfully applied to inkjet-printed OTFTs [25,39–41]. Inkjet-printed OTFTs based on blends of TIPS-pentacene with polymers such as polystyrene (PS) and polycarbonate have exhibited favorable mobilities of approximately 1 $cm^2 V^{-1} s^{-1}$, which is significantly higher than that of pure TIPS-pentacene. The blend films also contribute to a lower threshold voltage and reduced subthreshold swing. Typically, blending improves film uniformity, increases crystal coverage within the channel while reducing the variation of molecular orientation between crystalline domains. However, owing to the high viscoelasticity of long-chain polymers, the inkjet printing of their blends can be easily interrupted by clogging in the nozzle. To overcome this problem, Kjellander et al. have demonstrated an alternative approach by printing semiconductor ink onto a pre-deposited thin film of a soluble polymer [42]. The inkjet-printed droplet locally dissolves the polymer layer and forms a blend solution, thereby effectively controlling ink spreading and drying. However, the dependence of morphology and crystalline microstructures of the printed organic semiconductor on the solubility of the underlying polymer layer has not been clearly elucidated.

In this study, we utilize the photosensitive property of PS to control the crosslinking density and solubility of the polymer film by UV irradiation, thereby adjusting and optimizing the surface property of PS for the preparation of TIPS-pentacene by inkjet printing. Changes in the morphology and crystallization of TIPS-pentacene films, as well as the effect on the final device performance, were investigated with relation to surface solubility and wettability. An optimal PS film obtained with an appropriate UV dose was found to give the best interface modification for the inkjet-printed TIPS-pentacene film, which was confirmed by the electrical measurement of its OTFTs.

2. Experimental section

2.1. Materials

6,13-Bis(triisopropylsilylethynyl) pentacene (TIPS-pentacene) was purchased from TCI Chemical. Polystyrene (Mn = 140 kDa) and the solvent tetraline were purchased from Aldrich Chemical Co. All materials were used as received without further purification.

2.2. Preparation of crosslinked PS films

The silicon wafers were used as substrates, which were cleaned with acetone, ethanol and distilled water in sequence, then the substrates with hydrophilic bare surface were obtained by applying a UV-ozone treatment for 15 min. Polystyrene (Mn = 140 kDa) was spin-coated (3000 rmp, 60 s) from a 5 mg ml^{-1} solution in anhydrous toluene. The treated wafers were then baked on a 120 °C hot plate for 20 min to remove the residual solvent. The thickness of the PS films was 25 ± 0.5 nm measured by thin-film analyzer. And the capacitance of the PS-attached 300 nm SiO_2 dielectric was 10.6 nF cm^{-2}. The substrates were exposed under UV light (λ = 254 nm, power = 1.545 mW cm^{-2}) in nitrogen glove box for different time to manipulate the cross-linking degree of the PS films.

2.3. Inkjet printing of TIPS-pentacene

Inkjet printing was performed with a Dimatix DMP3000 printer in a 25 °C air-conditioned ambient environment with the relative humidity controlled at 40%. The temperature of the substrate was 28 °C. Tetralin (boiling point 207 °C, vapor pressure 0.056 kPa at 26 °C) was used as the solvent. TIPS-pentacene was dissolved in tetralin at a concentration of 20 mg mL^{-1} and injected into the cartridge equipped with 16 squarish nozzles through a 0.45 μm tetrafluoroethylene filter. Each nozzle of the jetting module, 21 μm in diameter, normally produces a 10 pL droplet in each ejection. The jetting frequency was fixed at 1 kHz in all printing process, and the jetting velocity was adjusted around 2.5 m/s. We have optimized the jetting parameters in order to make stable droplets with good repeatability and to remove satellite drops before printing onto the substrate.

2.4. Preparation of OTFT Devices

Scheme 1 schematically describes the fabrication of top-contact OTFTs on the UV cross-linked PS films. Firstly, heavily doped, n-type Si wafers with 300 nm thermal oxide (capacitance = 10.8 nF cm^{-2}) were carefully cleaned as above. The PS was spin-coated onto the silica. Then the crosslinked PS films were prepared by the exposure of UV light for different time. The TIPS-pentacene films were prepared by inkjet printing as semiconductor layers. A 60 nm thick Au layer was thermally evaporated and patterned through shadow masks (channel length = 90 μm,