Solar Energy Materials and Solar Cells 183 (2018) 137–145

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

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

Morphology and electrical characteristics of polymer: Fullerene films deposited by electrospray

Xin-Yan Zhao[a,b], Zui Tao[a], Weiwei Yang[b], Kaichen Xu[c], Lu Wang[d], Yuanyuan Jiang[e], Qianchen Zhang[a], Zhiqiang Gao[f], Baoxiu Mi[c,*], Minghui Hong[c,*], Weiwei Deng[b,*]

[a] Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Nanjing Tech University (Nanjing Tech), 30 South Puzhu Road, Nanjing 211800, China
[b] Department of Mechanics and Aerospace Engineering, Southern University of Science and Technology, Shenzhen 518055, China
[c] Department of Electrical and Computer Engineering, National University of Singapore, 4 Engineering Drive 3, 117576 Singapore, Singapore
[d] Key Laboratory for Organic Electronics & Information Displays (KLOEID), Jiangsu Engineering Centre for Plate Display & Solid State Lighting, Institute of Advanced Materials (IAM), Nanjing University of Posts & Telecommunications, Nanjing 210023, China
[e] Department of Mechanical Engineering, Virginia Polytechnic Institute and State University (Virginia Tech), Blacksburg, VA 24061, USA
[f] Key Laboratory of Flexible Electronics & Institute of Advanced Materials, Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), School of Material Science and Engineering, Nanjing University of Posts & Telecommunications, Nanjing 210023, China

ARTICLE INFO

Keywords:
Electrospray
Morphology
Polymer:fullerene
Electrical characteristics
Raman spectrum

ABSTRACT

Electrospray (ES) has emerged as an attractive approach to fabricate thin-film organic photovoltaic devices. However, the morphological properties and their implication to electrical characteristics of polymer:fullerene blends deposited by this method have not been clearly understood yet. In order to uncover the interplay of nanoscale morphology and electrical properties of ES-deposited films, both the residues of single droplets and thin films from the overlapping of multiple droplets were investigated by various characterization techniques. The surface morphology was demonstrated in details by the optical microscope (OM) and atom force microscope (AFM). The ordering structures and aggregation of the polymer were identified by the Raman and UV–vis spectroscopic investigations. The spatially distribution map of the P3HT aggregation states was analyzed by fitting the C=C mode of P3HT with Lorentzian functions. The conductive atomic force microscopy (C-AFM) was used to quantify local currents and reveal the correlation between the nanostructure and charge-transport mobility. Both surface morphology and aggregation of the P3HT were found to strongly depend on the overlapping boundaries formed by the dry residues of individual droplets. More P3HT aggregation present at the boundaries. However, boundaries also show significantly higher charge-transport resistance thus lower current. Thin films deposited with less droplet evaporation exhibit more homogenous morphology, more uniform phase segregation, and consequently higher charge mobility.

1. Introduction

Organic electronic devices have attracted much attention due to low-cost and abundant organic materials as well as the potential of flexible thin-film devices fabricated by roll-to-roll processes. Recently, the power conversion efficiency (PCE) of OPVs has exceeded 12% [1–3], mainly due to the development of novel polymers with small optical band gaps. Besides the breakthrough in new active materials and interface engineering, fabrication methods that are scalable, low-cost, and compatible with roll-to-roll manufacturing play a vital role for commercialization of organic electronic devices. To that end, technologies such as inkjet printing [4,5], screen printing [6,7], slot-die coating [8,9] and pneumatic spray coating [10–12] have been intensively investigated. Electrospray (ES), an electrohydrodynamic liquid atomizing technique, has emerged as an attractive approach to fabricate thin-film organic electronic devices such as organic light-emitting diodes (OLED) [13,14], organic thin-film transistors [15] and organic photovoltaics (OPV) [16–29]. Most recently, ES has been used to fabricate perovskite solar cells [30–32]. ES has unique advantages for organic thin films deposition for three reasons [33,34]: (i) the size of the quasi-monodispersity droplets is controllable from sub-micron range to about 100 μm; (ii) the uniform droplet size allows fine tuning of the active layer thickness and morphology; (iii) the charged droplet can be guided through electric field manipulation toward the substrate and thus result in virtually no material waste. ES-deposited organic photovoltaic devices (OPVs) achieving almost equal PCEs with spin

* Corresponding authors.
E-mail addresses: iambxmi@njupt.edu.cn (B. Mi), elehmh@nus.edu.sg (M. Hong), dengww@sustc.edu.cn (W. Deng).

https://doi.org/10.1016/j.solmat.2018.04.013
Received 18 January 2018; Received in revised form 8 March 2018; Accepted 11 April 2018

coating ones have been reported by our groups and other researchers [16–19].

One of the most remarkable features of OPVs is the use of the bulk heterojunction (BHJ) active layer forming by the blend of conjugated polymers and fullerenes, where intermixed phases provide donor/acceptor interfaces for exiton dissociation. After the exiton dissociation, the positive and passive charges transport toward the anode and the cathode through purer phases of polymer and fullerene, respectively. Therefore, the morphology of the blend active layer influences both the exciton dissociation and the charge transport, thus the optimization of the morphology is essential to increase efficiency for a particular set of materials. The morphology in polymer: fullerene blends deposited by spin coating has been intensively studied, and some consensus have been reached on how the three-phase network (intermixed, pure polymer and pure fullerene) could be controlled by the processing conditions such as pre-/post- annealing and additives [35–38]. However, corresponding investigation of the polymer: fullerene blend thin-film morphology deposited by other methodologies, especially the roll-to-roll compatible methods, are still lacking.

This work aims to systematically investigate the relationships between ES processing conditions, thin film morphology and electrical characteristics. ES process the thin film is formed by piling up of 'coffee rings' generated from individual droplets falling on the substrate, which is fundamentally different from the spin-coated films. To achieve high-efficiency devices, clear understanding of the nanoscale morphology and phase segregation properties of the ES-deposited polymer: fullerene thin film is important. We performed detailed studies for P3HT: PCBM, which is a classic blend system that serves as a benchmark model system for the general behaviour of polymer: fullerene thin films. The insights gained from this study will be transferable to other polymer: fullerene systems. Two types of samples are prepared: (i) the individual droplet deposition that forms isolated circular residue with thicker outer rims and thinner central regions; such patterns are often referred as coffee rings; and (ii) continuous films formed by overlapping and drying of multiple droplets. We will study the nanoscale morphology of the single coffee rings and continuous films, as well as the interplay between morphology and the electrical properties by various techniques such as the optical microscope (OM), atom force microscope (AFM) and Raman spectroscopy images.

2. Experimental

2.1. Film deposition

The typical electrospray deposition apparatus is shown in Fig. 1. The ES setup consists of a syringe pump, a DC high voltage power supply, a metal nozzle, and a hot plate placed on a motorized stage. The distance between the needle tip and the substrate was kept at 5 cm. A high voltage of 2.5–4 kV was applied between the nozzle and the substrate to generate stable electrospray in the cone-jet mode [16].

Patterned indium tin oxide (ITO) coated glass substrates were cleaned by sonication in a sequence of diluted Hellmanex solution, deionized (DI) water, acetone, and isopropyl alcohol (IPA) baths for 15 min each and then dried at 80 °C for more than 1 h prior to use. After drying, the substrates were treated by plasma for 45 s. Then the Poly (3,4-ethylenedioxythiophene) (PEDOT:PSS, CLEVIOS P VP AI 4083, Heraeus) solution was spin-coated onto the clean ITO/glass substrates under 3500 rpm for 60 s and annealed at 120 °C for 15 min. The Poly(3-hexylthiophene-2,5-diyl) (P3HT, Sigma Aldrich) and Phenyl C_{61} butyric acid methyl ester ($PC_{60}BM$, NanoC) with a weight ratio of 1:0.8 were dissolved in 1,2-Dichlorobenzene (DCB, Sigma Aldrich) at a concentration of 1.8 mg/ml, and the solution was stirred overnight at 45 °C in a glove box. As has been discussed in our previous work [16], to boost the electrical conductivity of the P3HT:PCBM solution, the acetic acid (Aladdin) was used as the additive (15 vol%) and the mixture was stirred for 1 h before ES. Then the solution was electrosprayed onto the PEDOT:PSS substrate. The P3HT:PCBM solution was injected through the nozzle at flow rates of 0.4, 0.7 and 1.1 ml/h and the substrate temperatures of 25, 40 and 90 °C, respectively.

For the spin coated reference samples, 20 mg P3HT and 16 mg PCBM were dissolved in 1 ml DCB, which was stirred overnight prior to use. The solution was spin coated on the PEDOT:PSS coated ITO/glass at 1000 rpm for 180 s and dried for more than 2 h in the glovebox.

2.2. Devices fabrication

The ES process was performed in air at room temperature. All samples were transferred in a thermal evaporator for metal electrode (Al of 100 nm) deposition at the pressure of 4×10^{-6} mbar. The active area of each device was 9 mm^2. Then the devices were post-annealed at 120 °C for 10 min in the glove box. The current density-voltage (*J-V*) characteristics were examined using a Keithley 2400 source measuring unit under simulated AM 1.5G illumination (100 mW cm^{-2}) with a

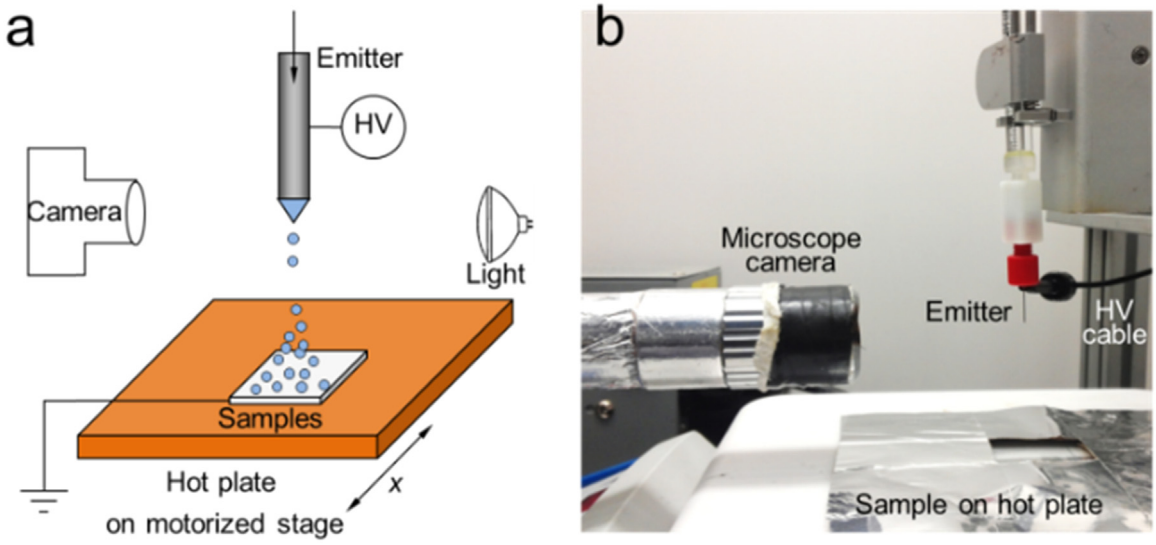

Fig. 1. (a) Schematic illustration of the electrospray setup, (b) photograph of the electrospray setup.