Organic Electronics 35 (2016) 118–127

Contents lists available at ScienceDirect

Organic Electronics

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

Inverted polymer bulk heterojunction solar cells with ink-jet printed electron transport and active layers

Arjun Singh [a, b, *], Shailendra Kumar Gupta [a, b], Ashish Garg [a, b, **]

[a] Department of Materials Science and Engineering, Indian Institute of Technology, Kanpur, Kanpur, 208016, India
[b] Samtel Centre for Display Technologies, Indian Institute of Technology, Kanpur, Kanpur, 208016, India

ARTICLE INFO

Article history:
Received 10 March 2016
Received in revised form
8 May 2016
Accepted 10 May 2016
Available online 20 May 2016

Keywords:
Organic solar cells
Ink-jet printing
Zinc oxide
Electron transport layer
Active layer
P3HT:$PC_{61}BM$

ABSTRACT

Ink-jet printing is a potentially attractive technique for printing of components for organic electronic devices primarily due to its ability to print patterned layers and reduced ink wastage. However, the mechanism of film formation is quite complex and needs an understanding of various printing parameters on the film growth. In this manuscript, we successfully demonstrate ink-jet printing of smooth zinc oxide (ZnO) thin films with controlled thickness as electron transport layers for inverted organic solar cell devices fabricated on indium tin oxide coated glass substrates. The parameters that strongly affect the formation of a continuous ZnO thin film with controlled thickness are ink concentration and viscosity, substrate surface treatment, drop spacing, substrate temperature during printing and the annealing temperature, affected by a combination of surface energetics, surface tension of the ink and the rate of solvent evaporation. The results suggest that one can achieve a transmittance of >85% for a 45 nm thin ZnO film possessing uniform structure and morphology, fabricated using a drop spacing of 40–50 μm at an ink viscosity of 4.70 cP with substrate held at room temperature. The P3HT:$PC_{61}BM$ inverted organic solar cell devices fabricated using printed ZnO films as electron transporting layers exhibit an efficiency of ~3.4–3.5%, comparable to that shown by the devices fabricated on spin coated ZnO films. Finally, the device with printed P3HT:$PC_{61}BM$ active layer on printed ZnO layer showed a device efficiency of *ca.* 3.2% suggesting that nearly completely printed devices can deliver a comparable performance to the spin coated devices.

1. Introduction

One of the attractive features of organic electronic devices is the feasibility of their fabrication by solution processing methods, in particular printing based methods offering enormous potential for large area fabrication of devices with reasonably high throughput [1–3] and hence possible reduction in costs. Whilst the blend of Poly(3-hexylthiophene-2,5-diyl) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) has been a workhorse system for bulk heterojunction (BHJ) organic solar cells, development of new low band-gap polymers and blend systems such as those based on Poly({4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl}{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl}) or PTB7 and Phenyl-C71-butyric acid methyl ester ($PC_{71}BM$) has seen laboratory scale device efficiencies exceed 10%. These OSC devices are typically fabricated in normal and inverted architectures on indium tin oxide (ITO) coated glass substrates with ITO acting as anode in normal devices and as cathode in inverted devices. Poor life times of normal organic solar cell devices primarily using hole transporting poly(3,4-ethylenedioxythiophene) polystyrene sulfonate) (PEDOT:PSS) layer on ITO electrode [4–6] and problems with the use of Al cathode [7] led to the development of inverted OSC devices. In inverted OSC devices, the hole transporting PEDOT:PSS layer between the active layer and ITO electrode is replaced by a thin electron transport layer (ETL), typically made of a n-type material such as zinc oxide (ZnO) or titanium dioxide (TiO_2) [8,9] with ZnO being a typical choice as ETL whilst another oxide such as molybdenum trioxide (MoO_3) [10,11] is used as a hole transport layer (HTL) between the active layer and the top electrode. Presence of stable oxides [12,13] at the electrode - active layer interfaces makes

* Corresponding author. Department of Materials Science and Engineering, Indian Institute of Technology, Kanpur, Kanpur, 208016, India.
** Corresponding author. Department of Materials Science and Engineering, Indian Institute of Technology, Kanpur, Kanpur, 208016, India.
E-mail addresses: arjunsin@iitk.ac.in (A. Singh), ashishg@iitk.ac.in (A. Garg).

http://dx.doi.org/10.1016/j.orgel.2016.05.015
1566-1199/

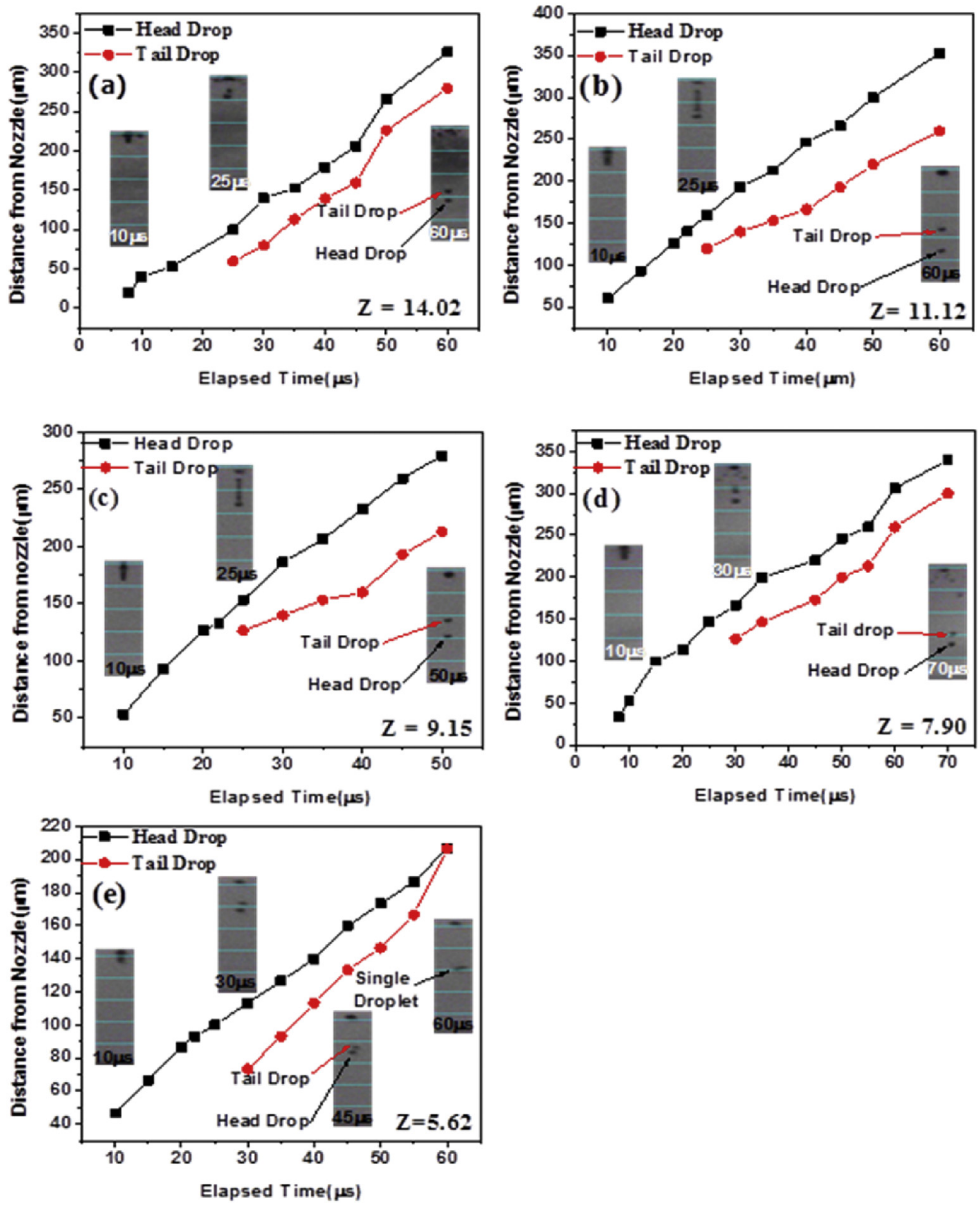

Fig. 1. Variation of drop shape vs elapsed time at a jetting voltage of 12 V for inks with different concentration (a) 0.25 M, (b) 0.35 M, (c) 0.45 M, (d) 0.55 M and (e) 0.70 M with Fromm number mentioned in each figure.

this inverted structure exhibit longer life times as compared to the normal OSC devices [14,15].

For mass production of OSCs, various printing methods are being considered. Among these, ink-jet printing, although not widely considered as a roll-to-roll process, is one of the attractive printing methods due to its ability to form patterned films eliminating or minimizing the need for lithography. Also, the technique offers superior control on the delivery of ink and its reduced wastage. Moreover, one can manipulate the speed of printing by employing multiple print heads and nozzles [16]. Ink-jet printing has been successfully explored for the deposition of common semiconducting polymeric materials such as PEDOT:PSS [17,18] and P3HT:$PC_{61}BM$ [19–24] for OSCs with devices yielding acceptable performances. However, the process of thin film formation in ink-jet printing is quite complex and is strongly affected by the parameters such as ink viscosity, drop spacing, substrate temperature and surface treatment, determined by the type of material.

From the perspective of inverted OSC device development by printing on ITO coated glass or plastic substrates, the first step has to be the printing of ZnO films followed by printing of active layer blend and other layers. However, in comparison to the printing of active layer blend and PEDOT:PSS, printing of oxides is a rather poorly addressed topic highlighting the need for detailed explorations. Specifically, in case of ZnO, whilst researchers have reported fabrication of ZnO in various forms such ZnO seed layer for nanorods [25], ZnO nanoparticles for gas sensors [26], amorphous oxides [27], zinc tin oxide [28–31], indium zinc tin oxide [28] and a few other oxides capped with nanoparticles using ink-jet printing method [32], none of these reports conclusively demonstrate the fabrication of ZnO films with controlled thickness which were further integrated into devices such as a working OSC device. Although there are recent reports on the ink-jet printing of ZnO for