



A transition solvent strategy to print polymer:fullerene films using halogen-free solvents for solar cell applications [☆]



Guan-Hui Lim ^{a,c}, Jing-Mei Zhuo ^{a,b}, Loke-Yuen Wong ^a, Soo-Jin Chua ^c, Lay-Lay Chua ^{a,b}, Peter K.H. Ho ^{a,d,*}

^a Department of Physics, National University of Singapore, Lower Kent Ridge Road, S117551, Singapore

^b Department of Chemistry, National University of Singapore, Lower Kent Ridge Road, S117543, Singapore

^c Department of Electrical and Computer Engineering, National University of Singapore, Lower Kent Ridge Road, S117576, Singapore

^d Solar Energy Research Institute of Singapore, National University of Singapore, Engineering Drive 1, S117574, Singapore

ARTICLE INFO

Article history:

Received 7 August 2013

Received in revised form 20 October 2013

Accepted 21 October 2013

Available online 2 December 2013

Keywords:

Organic solar cells

Ink-jet printing

Morphology

Solvent effects

Processing

ABSTRACT

Inkjet printing is a mask-less non-contact deposition technique that is potentially suited for prototyping and manufacturing of thin-film polymer organic semiconductor devices from digital images. However new strategies are needed to achieve films with good macromorphology (i.e., high-fidelity footprint and uniform cross-section) and nanomorphology on unstructured substrates using a conventional ink-jet. Here we report a new transition solvent strategy to provide the desired film macromorphology and ultrafine nanomorphology in regioregular poly(3-hexylthiophene):phenyl-C₆₁-butyric acid methyl ester (P3HT:PCBM) model films, without using chlorinated solvents. This strategy employs a good volatile solvent in combination with a miscible poor solvent that is much less volatile, which is the reverse of the usual low–high boiling-point solvent method. The good solvent suppresses premature aggregation in the ink head. Its removal by evaporation on the substrate leaves the poor solvent that triggers early π -stacking ordering and/or gelation of the polymer matrix that immobilizes the printed fluid on the substrate, suppressing both contact-line depinning and evaporation-induced solvent flow effects. The resultant donor–acceptor nanomorphology is further improved by vacuum drying at an optimal rate that avoids bubble formation. We have systematically characterized P3HT:PCBM films deposited with different solvents and platen temperatures to identify key macro- and nano-morphology determining processes. High-performance printed P3HT:PCBM solar cells were realized. These findings are applicable also to other printing and coating techniques based on low-viscosity inks.

© 2013 The Authors. Published by Elsevier B.V. All rights reserved.

1. Introduction

A key attractive feature of polymer organic semiconductor (OSC) devices is their processability over large and/or

flexible substrates using additive deposition methods, such as various printing and coating techniques [1]. Inkjet printing (ijp) offers some important advantages due to its non-contact operation, and ability to give patterned films with lateral resolution of better than 10 μm directly from digital image files at potentially very high speeds [2–8]. While the inkjet-printing of polymer OSC light-emitting layers in pre-formed confinement wells has reached advanced development, [9] the printing of field-effect transistors and solar cells is still in infancy and faces a number of challenges related to the drying-induced distortion of films that are not deposited into confinement wells [10–14].

[☆] This is an open-access article distributed under the terms of the Creative Commons Attribution-NonCommercial-No Derivative Works License, which permits non-commercial use, distribution, and reproduction in any medium, provided the original author and source are credited.

* Corresponding author at: Department of Physics, National University of Singapore, Lower Kent Ridge Road, S117551, Singapore. Tel.: +65 65168781.

E-mail address: phyhop@nus.edu.sg (P.K.H. Ho).

This problem is a consequence of the low viscosity in the “inks” printed by conventional *ijp*. As the solvent evaporates after deposition of the fluid puddle, the contact-line of the puddle retracts, which causes the footprint and position of the remaining fluid puddle to change. As the solvent evaporates further, materials deposition occurs and the contact line becomes pinned to the substrate. The puddle footprint now becomes fixed, but an evaporation-induced fluid flow towards the edge continues which piles up material to give a coffee-stain rim. These effects have been extensively studied for single printed droplets [15–20]. Other related phenomena, such as monolith formation [21] and buckling instability, [22] have also been documented in these films. When the droplets are arranged to give lines, new effects emerge, including droplet-bunching and line break-up [23–28]. When the droplets are arranged to give extended films, one can expect new complications from materials and solvent diffusion and from dissolution–recrystallization effects, [29] depending on how the droplets are arrayed. These latter phenomena have been much less studied. Even the basic features of how *ijp* processing parameters (temperature, solvent and drying conditions) affect the macromorphology of extended films are not well understood, despite their obvious importance to the free-form printing of transistor and solar cell films.

We report here a systematic study of *ijp* processing parameters on the macromorphology of the printed films using P3HT:PCBM as the materials model. We developed a transition solvent strategy that together with optimal vacuum drying enables “fixing” of the footprint and shape of the drying fluid puddle to give thin flat films with near uniform cross-section. The strategy employs a good volatile solvent in combination with a large fraction of a poor (not a bad!) but much less volatile solvent. This concept is opposite to the well-known strategy of combining a volatile solvent with a less volatile solvent which is also a good solvent for the OSC [11,12]. In that strategy, a rapid initial drying of the printed puddle is achieved to give a concentrated solution in a good solvent that then dries slowly to give the final film. Unfortunately this calls for the use of chlorinated aromatic solvents, usually a dichlorobenzene, for P3HT:PCBM and related materials systems, because only these solvents appear to have the required solvent power and high boiling points.

If however a volatile good solvent is combined with a much less volatile poor one, it should be possible to trigger early π -stacking and/or “gelation” of the polymer matrix on the deposition substrate by evaporation-induced quenching of the solvent quality rapidly through the borderline regime. Borderline solvents are known to induce formation of π -stacks of extended OSC polymer chains in solution to give well-ordered lamellae in neat films [30]. We show here that this strategy can simultaneously meet the twin goals of obtaining sufficient inkjet latency and dwell times (because of inclusion of the volatile good component), and surprisingly good macromorphology and nanomorphology of the printed films suitable for solar cell applications, without using chlorinated solvents. This approach is different also from the well-known use of

low-volatility solvent additives, usually a diiodoalkane or dithiol, at the few % level to prolong solvent annealing process of polymer:fullerene films [31].

We investigated P3HT:PCBM because this is an important model of OSC photoactive layer systems which comprise a semicrystalline π -stacking donor polymer in an intimate blend with a fullerene acceptor [32–36]. A mixture of 4:6 vol/vol toluene:*n*-butylbenzene was developed as the transition solvent, where toluene is a reasonably good solvent and *n*-butylbenzene is the poor solvent. This system produces films with better macro- and nano-morphologies than previously possible using a single-component non-chlorinated aromatic solvent, such as tetralene [11,12]. The critical challenge for a single-component non-chlorinated solvent is that it needs to simultaneously meet both the vapor-pressure and solvent-power requirements, which together constitute a formidable challenge for a semicrystalline polymer. For example, tetralene has a suitable vapor pressure for *ijp*, but is a poor solvent for P3HT. As a result, it severely depresses the inkjet latency and dwell times, and produces very rough films with coarse phase separations due to extensive π -stacking aggregation, even for a low regioregularity P3HT material [11,12].

The present strategy of incorporating a volatile good solvent component provides a new degree-of-freedom to overcome this challenge. We were thus able to inkjet print higher quality films with an improved power conversion efficiency, 2.2% vs 1.3% reported for tetralene. Although this is still poorer than those obtained from chlorinated aromatics (often by spin-casting), which is typically 3% at same composition and thickness, the difference may be narrowed by further optimization of the solvent mixture. Crucially the strategy here can avoid the use of halogenated solvents. Halogenated solvents are potential environmental concerns, and pose severe compatibility issues with printing tools, e.g., chlorinated aromatics are very harsh on the seals and plastic materials in the ink head and fluid delivery system. Amorphous polymers do not face as severe constraints [37]. This provides an important step towards the manufacture of polymer solar cell foils, and possibly also transistor films.

2. Experimental section

2.1. Substrate preparation

PEDT:PSSH (Baytron P, Leverkusen, Germany) was reformulated to give a 1:16 weight/weight (w/w) PEDT:PSSH material by dilution with PSSH [38,39]. 50-nm thick films were then spin-cast on glass or indium–tin oxide (ITO)–glass substrates. These films were annealed at 110 °C for 10 min (hotplate, N₂ glovebox) to remove residual moisture before P3HT:PCBM deposition.

2.2. Polymer:fullerene solution preparation

Regioregular P3HT (>97% regioregular, $M_n = 15$ –45 k; Plexcore OS 1100, Plextronics) and PCBM (Nano-C) were dissolved at the ratio of 1.5:1 weight-to-weight (w/w) into

Download English Version:

<https://daneshyari.com/en/article/10565971>

Download Persian Version:

<https://daneshyari.com/article/10565971>

[Daneshyari.com](https://daneshyari.com)