Probing film solidification dynamics in polymer photovoltaics

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A B S T R A C T

Semiconducting conjugated polymers have drawn a great deal of attention over the past decade due to their solution processability and potential use in roll to roll fabrication of organic solar cells. Here, we report the effect of solvent vapor pressure on poly(3-hexylthiophene):[6,6]-phenyl C_{61}-butyric acid methyl ester (P3HT:PCBM) blade coated inverted solar cells using ZnO as the electron transporting layer and MoO_3 as the hole transporting layer. The resultant morphology and device performance are investigated for devices processed from solvents with varied vapor pressure and a mixed solvent. We report that the use of a mixed solvent system is advantageous for controlling the initial vapor pressure of the processing solution, thereby controlling the phase separated morphology between P3HT and PCBM which impacts ultimate solar cell performance.

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1. Introduction

As reported by the U.S. Energy Information Administration, world energy consumption is expected to grow 56% from 2010 to 2040. The fastest growing segments of the energy market are renewables and nuclear, which are expected to increase by 2.5% per year [1]. As the global demand for energy increases, new, innovative ways to meet those demands in a cost effective, sustainable manner are essential and imperative. Further, technologies having a low carbon footprint are desirable. One attractive, emerging renewable energy technology that offers the potential to meet all the desired attributes is broadly represented by solar, organic and hybrid photovoltaics (OPVs) in particular. OPV utilizes highly tunable materials; single junction devices based upon small molecules have achieved efficiencies approaching 9% [2,3], while polymeric materials have afforded cells with power conversion efficiencies (PCEs) higher than 9% [4,5].

Substantial efforts have been focused towards materials design and synthesis to produce novel small molecule and polymeric materials that will yield devices with optimized performance attributes, power conversion efficiency (PCE) in particular [6]. However, until recently, a quantitative understanding of how materials processing impacts device characteristics has lagged behind efforts to identify alternative molecular structures. While

the design and synthesis of materials that afford high PCE's and demonstrate good stability is important, the ability to process those materials into integrated large-scale OPV systems, while maintaining optimum device performance, may well be the defining element to the success of OPV technology [7].

The most readily available laboratory-based process methodology used in the fabrication of thin polymer films is spin coating, and this technique is the one most commonly used to fabricate OPV devices in a research environment. However, spin coating is not viable for either the manufacture of large-area or flexible devices. Further, and perhaps more importantly, the critical process parameters that control thin-film morphology will be substantially different for films prepared via spin coating vs. alternative methods such as spray coating [8,9], slot die coating [10], ink jet printing [11], and blade coating [12–21], which makes it critical to investigate these various large scale processing techniques. While the final morphology and its evolution during spin coated film formation has been extensively studied, investigations associated with blade coating have lagged behind, even though it is especially well-suited for ultimate comparison to roll-to-roll (RtR) manufacturing processes [22,23]. The impact of the active layer deposition process is aptly demonstrated in a report by Brabec and co-workers who showed that the thin-film morphology obtained upon blade vs. spin coating active layer thin-films is markedly different, with blade coating affording higher open circuit voltage (V_{oc}) [13].

An additional principal consideration related to OPV device fabrication pertains to the ability to integrate the active layer

thin-film deposition method with low-cost, high through-put, large-area fabrication via RtR production. While solution processed OPV's can be realized using RtR methods, to be commercially viable, a sound knowledge base regarding critical process parameters associated with RtR compatible solution processed materials for solar cell devices is an imperative, as is knowledge concerning the impact and control of resultant morphology. Fundamentally then, we ask "*How do we bridge the processing gap?*", and move away from spin coating to RtR compatible processing methods for large area high efficiency OPVs?

Here, blade coating was used to fabricate the active layer of inverted solar cells from a solution of poly(3-hexylthiophene-2,5-diyl) and [6,6]-phenyl C_{61} butyric acid methyl ester(P3HT/$PC_{60}BM$) to identify and investigate the critical process parameters associated with the fabrication of OPVs via blade coating of the active layer. A series of common chlorinated processing solvents, which have a difference in vapor pressure over a range of three orders of magnitude, were selected to examine solvent effects, such as evaporation rate, on ultimate morphology and device performance. Solvents such as chlorobenzene, *ortho*-dichlorobenzene and toluene are commonplace in OPV fabrication [14–17], however, their impact on the performance of blade coated devices has not been investigated. Since the kinetic and thermodynamic phenomena associated with blade coating will differ substantially from the largely kinetically driven processes operational during spin coating, it is essential to elucidate the role of the solvent in the former approach to OPV device fabrication [24].

Bulk-heterojunction inverted solar cells were fabricated using P3HT (>98% head to tail) and $PC_{60}BM$ in anhydrous chloroform (CF), chlorobenzene (CB), *ortho*-dichlorobenzene (DCB) and trichlorobenzene (TCB) as the deposition solvent. These four solvents exhibit significant vapor pressure differences of approximately one order of magnitude between each at room temperature, which facilitates investigation of the effects of deposition solvent characteristics, solvent vapor pressure in particular, on active layer thin-film morphology and ultimately device performance.

2. Results and discussion

2.1. Solvent analysis

The physical characteristics of the four solvents (CF, CB, DCB, TCB) used in this investigation are shown in Table 1. The solvents were selected based upon wide differences in vapor pressure and boiling point: the former ranges from a high of just over 190 mmHg to a low of approximately 0.3 mmHg for CF and TCB, respectively, while boiling point spans from 61 to 214 °C. The boiling point and vapor pressure differences will affect blade coated thin-film drying time, which in turn will impact both morphology and device characteristics, thereby facilitating correlation of device properties with process solvent attributes. It is hypothesized that

an increase in drying time through the use of low vapor pressure solvent, will allow for development of an optimum nanoscale phase morphology and will correlate with high device efficiencies.

The inherent solubility characteristics of a deposition solvent may also be expected to affect the film deposition process. One measure of solubility derives from the Hansen solubility parameters (HSP), which provide insight into polymer/solvent mixing through calculated thermodynamic characteristics of the media. As seen from the data in Table 1, P3HT:$PC_{60}BM$ solubilizes well in the four chlorinated solvents under investigation [25]. While HSP analysis can be a useful tool to evaluate the solubility of specific components and impacts ink formulations, kinetic factors play a large and influential role, thereby ultimately regulating morphology and device performance [26]. Factors such as vapor pressure and/or boiling point will bear directly on the kinetics of film formation.

2.2. Blade coated P3HT:PCBM solar cell characteristics

Fig. 1 and Table 2 show the current density (mA/cm^2) vs. voltage (V) (J–V) characteristics of inverted solar cells fabricated via blade coating the active layer under ambient atmosphere. In this study, inverted solar cells were fabricated starting with cleaned indium tin oxide (ITO) substrates onto which ZnO sol–gel was spin coated and annealed in air to form a semi-transparent electron transporting layer. P3HT:$PC_{60}BM$ was blade coated onto the ZnO layer in air and allowed to dry. Devices were then brought into a glovebox where they were thermally annealed at 140 °C for 35 min followed by thermal evaporation of 4 nm of MoO_3, which serves as a hole-transporting layer, and 100 nm of Ag. The inverted architecture was used due to the higher air stability of inverted devices vs. conventional structures brought by the higher work function a Ag (4.73 eV) electrode relative to Ca (2.9 eV) and Al (4.08). Electrons are collected at the ITO interface while holes are collected at the Ag electrode. Incorporating this geometry also circumvents using poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) on ITO which is reported to hinder device performance due to chemical instabilities at the interface [27]. Average solar cell characteristics were determined in order to more accurately represent the experimental data [28], with typically 8 devices tested for each set of conditions.

The impact of solvent on device performance is readily apparent: J_{sc} increases with the solvent sequence CF to CB to DCB, yet a significant drop in J_{sc} is observed with TCB (~10.5 mA/cm^2 for DCB processed devices vs. ~8.7 mA/cm^2 those using TCB). Film thickness (~160 nm), as determined using profilometry (Fig. S1) was the same for all devices investigated here. The absence of a C–Cl stretch at 600–800 cm^{-1} in the FT-IR spectra of coated films confirmed that solvent was essentially absent (Fig. S2), and thus residual solvent is not a relevant factor. Open circuit voltage (V_{oc}) was similar for devices fabricated using CF, CB and DCB, but was slightly higher for TCB processed cells. Fill factor (FF%) and PCE% increased with

Table 1
Characteristics of solvents investigated for blade coating P3HT:PCBM thin films: properties that influence polymer–solvent interactions and drying kinetics in polymer solutions and films.

Solvent	Vapor pressure at 25 °C (mmHg)	Boiling point (°C)	Hansen solubility parameters[b]			[a]P3HT solubility (mg/mL)	[b]PCBM solubility (mg/mL)
			δ_D (MPa$^{1/2}$)	δ_P (MPa$^{1/2}$)	δ_H (MPa$^{1/2}$)		
Chloroform (CF)	193.5	61.2	17.8	3.1	5.7	34	28.8
Chlorobenzene (CB)	11.8	131	19	4.3	2	15	59.5
Dichlorobenzene (DCB)	1.47	180.5	18.3	7.7	2.8	21	42.1
Trichlorobenzene (TCB)	0.29	214.4	20.2	4.2	3.2	18	81.4

[a] Solubility of P3HT determined experimentally.
[b] HSP parameters and solubility taken from Ref. [25].