Solar Energy Materials & Solar Cells 98 (2012) 118–123

Contents lists available at SciVerse ScienceDirect

Solar Energy Materials & Solar Cells

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

Inverted semi-transparent organic solar cells with spray coated, surfactant free polymer top-electrodes

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ARTICLE INFO

Article history:
Received 21 August 2011
Received in revised form
6 October 2011
Accepted 7 October 2011
Available online 6 November 2011

Keywords:
Organic solar cell
Spray coating
Conductive polymer
Polymer electrode
Organic semiconductor coating

ABSTRACT

Depositing a poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) buffer layer or top-electrode from aqueous solution on a non-polar active layer in inverted organic solar cells is commonly considered a very challenging task. In this work we utilize spray deposited PEDOT:PSS seeds to effectively reduce the surface free energy atop the active layer in poly-hexylthiophene polymer solar cells before applying a PEDOT:PSS top-electrode. Though aqueous PEDOT:PSS is repelled from non-polar surfaces, very small droplets can adhere to the surface. The distribution of the sprayed PEDOT:PSS droplets can be controlled via the substrate temperature and the material flow rate. The less time the droplets have to contract along the surface before drying, the better is the surface seed coverage and the more homogenous is the formation of a subsequently deposited PEDOT:PSS electrode. The respective solar cells are semi-transparent and exhibit an overall power conversion efficiency $\eta \approx 2\%$.

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1. Introduction

Polymer solar cells are a gradually maturing technology with power conversion efficiencies now exceeding 9% [1]. While the efficiencies of such solar cells will continue to improve, the true economic viability of these devices will only be realized through the concurrent advancement of inexpensive fabrication technologies. Accordingly, several in-line fabrication-compatible printing and coating technologies have been investigated, including gravure printing, doctor blading, inkjet printing, slot die coating and spray coating [2–4]. The latter has drawn a lot of attention as spray coating combines the advantages of an easily scalable and mature process with low investment costs. There have been reports of bulk heterojunction organic solar cells based on spray coated poly(3-hexylthiophene-2,5-diyl) and [6,6]-phenyl C_{61}-butyric acid methyl ester (P3HT:PCBM) with power conversion efficiencies exceeding 4% [5–7] and active areas of more than 12 cm^2 [8]. Spray coated charge carrier transport layers of poly(3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS) have also been examined [9]. As PEDOT:PSS can exhibit conductivities of up to 1400 S/cm, it is suitable for standalone transparent anodes [10–12] and cathodes [13]. It can also act as a top electrode or as part of this electrode in the industrially more relevant inverted device architecture [14]. The conductivity of PEDOT:PSS electrodes can be improved further by supporting metal grids [15]. Unfortunately, as PEDOT:PSS usually comes in aqueous solution, it exhibits very poor wetting properties on a non-polar P3HT:PCBM surface or any other non-polar organic layer. Normally, PEDOT:PSS wetting is improved by additives such as fluorinated surfactants and/or solvents with surface energies comparable to the surface energy of the underlying surface [16,17]. However, the surfactants remain in the PEDOT:PSS layer and so must be chosen carefully. Alternatively, poly(allylamine hydrochloride) and dextran (PAH-D) can be used to modify the P3HT:PCBM surface polarity and to allow PEDOT:PSS wetting [18]. A similar approach is to wet the surface with isopropanol while at the same time some isopropanol is added to the PEDOT:PSS solution [19]. Without giving process details, Weickert et al. proposed the use of spray coated PEDOT:PSS seeds on a P3HT:PCBM surface to allow a subsequently spincast (low-conductive) PEDOT:PSS layer to wet the originally non-polar surface [20].

In this work we present a fully spray coated and highly conductive polymer top-electrode in an inverted polymer solar cell. By comprehensively investigating PEDOT:PSS seeding, i.e. systematically changing the P3HT:PCBM surface free energy, we avoid the utilization of any surfactants when depositing a spray cast PEDOT:PSS top electrode.

2. Experimental details

For the fabrication of inverted polymer solar cells as depicted in Fig. 1 we utilized structured ITO substrates that were cleaned in

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doi:10.1016/j.solmat.2011.10.016

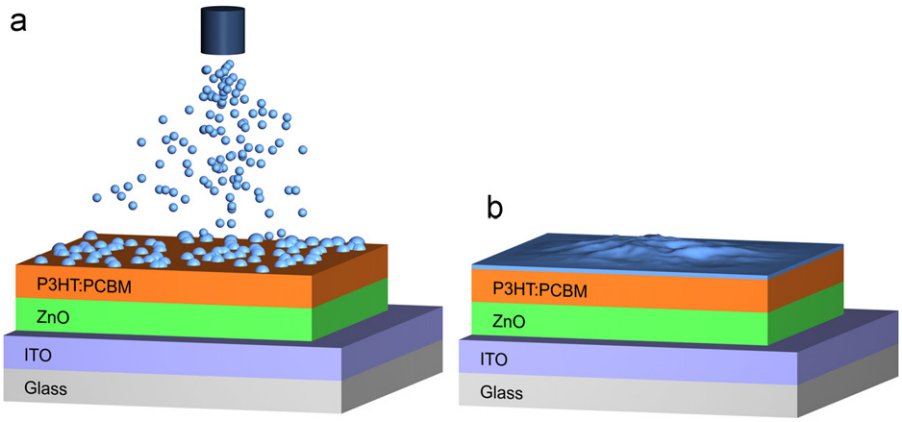

Fig. 1. Device architecture and fabrication process: (a) seed spray coating on P3HT:PCBM surfaces with low material flow rates in order to avoid dewetting, (b) subsequent application of a PEDOT:PSS wet film atop the seeds with high material flow rates in order to form a wet film and to ensure a more uniform coverage and hence to build a conductive top electrode.

isopropanol for 15 min. Before spincasting the zinc oxide buffer layer we spin-rinsed the sample with ethanol. As an advancement of the process described in Ref. [21], the zinc oxide layer was deposited via spincoating from a filtered, 100 °C, 20 mg/mL zinc acetylacetonate hydrate/ethanol solution. The hot solution was applied on a rotating sample that was subsequently annealed for 60 s at 120 °C. According to atomic force microscope images (data not shown here) the surface roughness R_a of the zinc oxide layer is well below 10 nm. P3HT:PCBM (1:0.9 blend ratio, 40 mg/mL solid content) was spincast from a dichlorobenzene solution resulting in a 180 nm thick active layer. PEDOT:PSS Clevios PH1000 from Heraeus Clevios GmbH was formulated by adding 10 vol% of the high boiling solvent dimethylsulfoxide in order to achieve high PEDOT:PSS conductivities, and 10 vol% isopropanol for better wetting on the P3HT:PCBM surface. No surfactants were added to the PEDOT:PSS formulation. For the deposition of the PEDOT:PSS, we utilized a Sono-Tek spray coater with an ultrasonic atomizing nozzle system that allows adjustment of the PEDOT:PSS droplet sizes by altering the ultrasonic frequency. In a first step, PEDOT:PSS seeds were applied to P3HT:PCBM surfaces heated to 20 °C, 50 °C or 80 °C by spraying PEDOT:PSS for 60–300 s at a rate of 0.04 mL/min and a pressure of 2.8 psi. In a second step, the flow rate was increased to 0.7 mL/min and a PEDOT:PSS wet film was spray deposited for 18 s on the modified surfaces. Deposition through a shadow mask during this step enabled the formation of the counter electrode upon drying.

Contact angles were measured utilizing a KSV goniometer under ambient conditions. Surface free energies were calculated from static contact angles of the solvents glycerin, DMSO and water with the sample surface according to the procedure described by Owens et al. [22].

While all processing steps were carried out in air, we characterized the solar cells under illumination from an Oriel 300 W solar simulator after annealing under a nitrogen atmosphere.

3. Results and discussion

3.1. Deposition of PEDOT:PSS seeds

Deposition of PEDOT:PSS onto non-polar surfaces is problematic due to a mismatch of their surface free energies. In order to circumvent this problem, here we systematically changed the surface free energy by spraying a PEDOT:PSS/DMSO/isopropanol formulation at a low flow rate onto the ITO/ZnO/P3HT:PCBM sample before applying the wet film, that later forms the conductive electrode. If a wet film forms on the P3HT:PCBM surface at this stage of the process, PEDOT:PSS will not adhere to the non-polar active layer but drop off the surface. Accordingly, a certain spray coating rate must not be exceeded in this very first application step. If the material flow is kept low (0.04 mL/min), the droplets dry on the surface and form little PEDOT:PSS islands or "seeds". Due to this PEDOT:PSS island formation on the P3HT:PCBM surface, the change in surface free energy comes at the cost of an increased surface roughness. Besides the material flow rate, the PEDOT:PSS seed distribution can be improved by increasing the spray time and the substrate temperature. The latter leads to faster evaporation of the solvent in the PEDOT:PSS formulation, causing the droplets to dry immediately upon contacting the P3HT:PCBM surface. Fig. 2 shows atomic force micrographs of PEDOT:PSS seeds that were sprayed on 20 °C, 50 °C and 80 °C hot P3HT:PCBM surfaces for 3 min. While the droplets on 20 °C P3HT:PCBM surfaces have time to diffuse and coalesce, the droplet shapes become more and more pronounced at higher substrate temperatures. On a larger scale, this change in drying behavior leads to a higher surface coverage that is even more pronounced for longer spraying times and hence for larger amounts of PEDOT:PSS sprayed onto P3HT:PCBM. Fig. 3 shows greyscale photographs of the PEDOT:PSS network formed on P3HT:PCBM surfaces for different spraying times and substrate temperatures. While the droplets are distributed more uniformly at higher substrate (drying) temperatures, the PEDOT:PSS contracts on 20 °C P3HT:PCBM surfaces and forms structures of a distinctive size due to the different surface energies of P3HT:PCBM and PEDOT:PSS. A more quantitative analysis can be conducted by performing a two-dimensional discrete Fourier transform (2D-DFT) of the PEDOT:PSS structures. The radially averaged isotropic representations of the 2D-DFTs are depicted in Fig. 4. At a substrate temperature of 20 °C we find a predominant spatial wavelength of about 50 μm that becomes more pronounced with a longer spray time or an increased amount of PEDOT:PSS, respectively. This predominant spatial wavelength in the 2D-DFT is related to the formation of distinctive structures due to PEDOT:PSS droplet migration on the P3HT:PCBM surface (Fig. 4a) as already observed in Fig. 3. When increasing the substrate temperature to 50 °C or further to 80 °C, the feature in the 2D-DFT at 50 μm spatial wavelength almost vanishes, indicating a reduced migration and hence a much more uniform distribution of the PEDOT:PSS droplets.

3.2. Surface property analysis

For an analysis of the surface properties we converted the micrographs in Fig. 3 into black and white images, defining the histogram minimum between the bright and dark area peaks for

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