Simultaneous multilayer formation of the polymer solar cell stack using roll-to-roll double slot-die coating from water

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ABSTRACT

Double slot-die coating using aqueous inks was employed for the simultaneous coating of the active layer and the hole transport layer (HTL) in fully roll-to-roll (R2R) processed polymer solar cells. The double layer film was coated directly onto an electron transport layer (ETL) comprising doped zinc oxide that was processed by single slot-die coating from water. The active layer comprised poly-3-hexylthiophene:Phenyl-C_{61}-butyric acid methyl ester (P3HT:PCBM) as a dispersion of nanoparticles with a radius of 46 nm in water characterized using small-angle X-ray scattering (SAXS), transmission electron microscopy (TEM), and atomic force microscopy (AFM). The HTL was a dispersion of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) in water. The films were analyzed using time-of-flight secondary ion mass spectrometry (TOF-SIMS) as chemical probe and X-ray reflectometry as physical probe, confirming the identity of the layered structure. The devices were completed with a back electrode of either Cu tape or evaporated Ag. Under standard solar spectrum irradiation (AM1.5G), current–voltage characterization (J–V) yielded an open-circuit voltage (V_{oc}), short-circuit current (J_{sc}), fill factor (FF), and power conversion efficiency (PCE) of 0.24 V, 0.5 mA cm^{-2}, 25%, and 0.03%, respectively, for the best double slot-die coated cell. A single slot-die coated cell using the same aqueous inks and device architecture yielded a V_{oc}, J_{sc}, FF, and PCE of 0.45 V, 1.95 mA cm^{-2}, 33.1%, and 0.29%, respectively.

1. Introduction

Flexible polymer solar cells can be manufactured by roll-to-roll (R2R) processes, which are inherently faster than batch processing of solar cells [1]. The manufacture of polymer solar cells using R2R processing has been reported demonstrating high speed of manufacture even on a small scale [2–4]. Thus, polymer solar cell modules with the size of an A4 sheet of paper have total processing times in the range of one minute (45–90 s) [3]. This period of time is from the moment the fresh carrier substrate enters the process until the completed, encapsulated, and tested polymer solar cell module exits the process as a finished product. It is impossible to envisage such throughput speeds with any process that handles the solar cell as a discrete unit. The above example employed relatively simple R2R processing equipment and low web speeds in the range of 0.3–2 m min^{-1} processing one layer at a time by subsequent single passes through the machinery. In order to improve throughput speed there are a few

routes, which can be followed. One obvious route is to increase the processing speed, which puts significant requirements on the drying equipment. The faster the web speed, the larger and more complex the ovens and driers become. Another option is to make an inline printing and coating machine where the same web passes through several printing stations with each station representing each layer in the solar cell stack. This method has the advantage of minimizing handling damage of the web. The method does put some constraints on the chosen printing and coating methods as they all have to operate in the same window of web speed and the final web speed will be determined by the slowest process. A final route is the simultaneous formation of several layers of the solar cells stack. This method is in many ways ideal as it lowers the number of passages through the processing equipment thus lowering the handling damage, increases the processing speed significantly without increasing the web speed and thus does not necessarily require more complex drying technology. In addition, there are advantages in the context of life cycle analysis and the method provides a path to a reduction of the energy payback time (EPBT) by significantly reducing the direct process energy involved in the manufacture [5]. The approach also introduces a massive challenge in
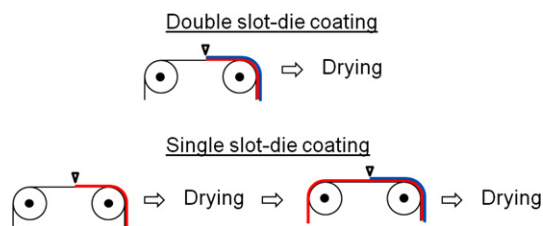
Fig. 1. Illustration of the double slot-die coating of the active layer (red) and the HTL (blue) in a R2R process, compared to the equivalent process using single slot-die coating. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

the ink formulation for the layers that are coated simultaneously as the formation and drying of a wet multilayer film is highly complex. The successful application of the technique is however rewarding in terms of processing speed and simplicity, see Fig. 1.

In this work we demonstrate the simultaneous formation of two of the layers in the polymer solar cell stack by double slot-die coating of the active layer and the hole transporting layer (HTL) from aqueous dispersions. We describe the ink formulation and the required steps to efficiently design inks that give stable bilayer structures in the wet film and during drying.

2. Experimental

2.1. Materials

P3HT (Sepiolid P-200 from BASF) was employed as the donor polymer and technical grade PCBM was employed as the acceptor material (Solenne BV). An aqueous precursor solution for the ZnO was prepared as described earlier [6] and comprised $Zn(OAc)_2.2H_2O$ (100 mg mL^{-1}), $Al(OH)(OAc)_2$ (2 mg mL^{-1}), and the non- ionic fluorosurfactant (FSO-100) (2 mg mL^{-1}) in water. PEDOT:PSS was based on an aqueous dispersion (2:1 w/w) of Orgacon EL-P 5010 from Agfa that was used directly as received. The electrode material was either Cu tape or evaporated silver. The substrate was a 130 µm poly(ethylene terephthalate) (PET) substrate with a patterned ITO layer (nominally 60 Ω square^{-1}) (acquired from IST).

2.2. Nanoparticle preparation and ink

P3HT (4 g, Sepiolid P200, BASF) and PCBM (4 g, 99%, Solenne B.V.) were dissolved in chloroform (268 g, Spectrophotometric grade, Sigma-Aldrich) and mixed with an aqueous 100 mM sodium dodecyl sulfate (SDS) solution (480 mL) (99%, Sigma-Aldrich) in a large beaker. The mixture was stirred vigorously for one hour and then subjected to ultrasound (0.9 kW) for 6.5 min using an UIP 1000 hd transducer from Hielscher ultrasound technology fitted with a booster head. The mixture was then stirred on a hot plate at 65 °C for three hours until all the chloroform had evaporated. The aqueous dispersion was dialyzed to remove SDS using a Millipore system with a capacity of 500 mL. The mixture was concentrated by dialysis from a volume of 500 mL to a volume of 100 mL with a forward pressure of 1.4 bar and a pressure gradient across the filter of 0.7 bar. Pure water (400 mL) was then added and the procedure was repeated 4 times corresponding to a dilution of the solution by a factor of 625. In the final step the suspension were concentrated to have a solid content of 60 mg mL^{-1}. FSO-100 was added to the dialyzed aqueous suspension of the P3HT:PCBM nanoparticles. The concentration of fluorosurfactant was 5 mg mL^{-1} and the P3HT:PCBM concentration was 60 mg mL^{-1}. This solution was employed directly for slot-die coating.

2.3. TOF-SIMS

Depth profiling analysis was performed using a TOF-SIMS IV (ION-TOF GmbH, Münster, Germany). 25-ns pulses of 25-keV Bi$^+$ (primary ions) were bunched to form ion packets with a nominal temporal extent of < 0.9 ns at a repetition rate of 10 kHz yielding a target current of 1 pA. Depth profiling was performed using an analysis area of 100×100 µm^2 and a sputter area of 300×300 µm^2. 30 nA of 3-keV Xe$^+$ was used as sputter ions. Electron bombardment (20 eV) was used to minimize charge build-up at the surface. Desorbed secondary ions were accelerated to 2 keV, mass analyzed in the flight tube, and post-accelerated to 10 keV before detection.

2.4. SAXS

The X-ray source for the SAXS measurements was a Cu rotating anode (Rigaku H3R), collimated and monochromatized by 2D multilayer optics (K_α radiation, $\lambda = 1.5418$ Å). The anode was operated in fine focus mode at 46 kV/46 mA and the beam diameter was collimated by 3 pinholes to 1.0 mm diameter at the sample position. An 18×18 cm^2 2D position sensitive gas detector was used for collecting the scattering data, and a 4 mm beamstop was placed in front of the gas detector, situated 4579 mm from the sample.

2.5. Reflectrometry

The reflectrometry measurement was made on setup with a rotating Cu-anode (Rigaku RU-200) operated at 50 kV/200 mA as X-ray source, focused and monochromatized by a 1D multilayer optic (K_α radiation, $\lambda = 1.5418$ Å).

2.6. AFM

The P3HT:PCBM nanoparticle dispersion was spin-coated on a glass substrate. The AFM imaging was performed on an N8 Neos (Bruker Nano GmbH, Herzogenrath, Germany) operating in an intermittent contact mode using PPP-NCLR cantilevers (NANO-SENSORS, Neuchatel, Switzerland). The images were recorded at a scan speed of 0.8 lines s^{-1}.

2.7. Substrate preparation

A PET substrate with an ITO pattern was prepared and cleaned as described earlier [2]. The ZnO solution was microfiltered immediately prior to use (filter pore size of 0.45 µm) and then slot-die coated at a speed of 2 m min^{-1} with a wet thickness of 4.9 µm. After the initial drying of the precursor film it was converted into an insoluble film by passage through an oven at a temperature of 140 °C with a speed of 0.2 m min^{-1} (oven length = 4 m). This gave an insoluble doped zinc oxide film with a thickness of 25 ± 5 nm.

2.8. Double slot-die coating

The web was forwarded at a speed of 1 m min^{-1} when the aqueous P3HT:PCBM nanoparticle dispersion was pumped into the first chamber of a double slot-die coating head. The aqueous PEDOT:PSS dispersion was pumped into the second chamber of the double slot-die coating head. The double film was then slot-die coated at a nominal wet thickness of 23 µm for both the P3HT:PCBM film and the PEDOT:PSS dispersion. The slot-die coating head and the coating roller had temperatures of 60 °C and 80 °C, respectively. The temperature of the foil was kept at