Solar Energy Materials & Solar Cells 144 (2016) 724–731

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

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

Fully gravure printed organic photovoltaic modules: A straightforward process with a high potential for large scale production

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ARTICLE INFO

Article history:
Received 18 August 2015
Received in revised form
14 October 2015
Accepted 17 October 2015
Available online 11 November 2015

Keywords:
Flexible organic photovoltaics
Gravure printing
Module
P3HT:PCBM bulk heterojunction
Spectroscopic ellipsometry

ABSTRACT

In this work, we describe a novel approach for the fabrication of flexible organic photovoltaic (OPV) modules with an inverted architecture by a versatile and scalable gravure printing process. The printing has been carried out using a sheet-to-sheet (S2S) lab scale proofer, while all the printing steps were performed in ambient conditions and were optimized for each of the OPV layers. Commercially available zinc oxide (ZnO) ink was used as the electron transport (ETL) layer, poly(3-hexylthiophene):[6,6]-phenyl C61 butyric acid methyl ester (P3HT:PCBM) blend comprised the bulk heterojunction (BHJ) photoactive layer, poly-3,4-ethylenedioxy-thiophene:poly(styrenesulfonic-acid) (PEDOT:PSS) was used as the hole transport layer (HTL), and silver (Ag) nanoparticle ink was used as the top contact electrode. The four OPV layers have been successively printed on indium tin oxide (ITO) coated polyethylene terephthalate (PET) flexible substrate using the same printing parameters, allowing the high production throughput in a roll-to-roll (R2R) printing process. The printed OPV modules have size of 45 cm^2 with an active area of 8 cm^2 composed of 8 interconnected cells and exhibited a maximum power conversion efficiency (PCE) of 2.22%. The printing parameters were optimized by the contribution from extensive morphological characterization carried out by scanning and transmission electron microscopy (SEM, TEM), as well as from Spectroscopic Ellipsometry (SE) for the determination of the printed layers thickness, optical properties and photoactive layer blend morphology. The above approach revealed the required printing parameters for the further optimization of the layer interface, morphology, thickness and substrate properties in order to implement the above methodology for large-scale manufacturing of flexible OPVs by a R2R process.

1. Introduction

Organic photovoltaic devices (OPVs) fabricated by wet processes are an emerging field of research since they exhibit a tremendous potential for large area, lightweight and conformable devices fabricated by low-cost production processes. It was since 1986 when Tang et al. [1] reported for the first time the fabrication of a two-layer OPV cell, while, a lot of research studies have been carried out with a continuous progress of the device efficiency utilizing new materials, device engineering and device physics [2–7]. Spin coating is the dominant method for the lab-scale construction of small-scale OPVs [8]; however, in order to transfer the fabrication process to mass production of large area OPV modules other techniques have to be used [9,10]. This could enhance apart from the OPV total active area the total energy output. To that end, a lot of research is conducted in printing techniques that enable high-volume and large area OPV production; such as ink-jet, screen, knife-over-edge, spray coating, gravure, and slot die [11–31].

The power conversion efficiency (PCE) of the state-of-the-art OPVs consisting of a donor/acceptor bulk heterojunction (BHJ) active layer or tandem structures can reach over 10% [32,33]. Some printed devices connected in parallel have been fabricated, and the various module formulations demonstrated their ability to be integrated with other electronic devices enabling printed OPVs with a commercial potential for energy harvesting [34–40]. Currently, the development of fully-printed OPV modules, including the top metal electrode; in most cases vacuum-deposited Al or Ag

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http://dx.doi.org/10.1016/j.solmat.2015.10.021
0927-0248/

electrodes, is one of the most essential targets in the field of OPVs because all processing and production limitations should be overcome [41–43].

Gravure printing has been widely used in the commercial manufacture of packaging, decorative papers, magazines, currency, etc., and is an attractive technique for manufacturing printed electronics because it offers the advantages of high-throughput, high-quality printing with high resolution [44,45]. It can deliver high printing speeds and film thicknesses that are appropriate for OPVs [23,24]. Gravure printed films can be optimized by adjusting the printing parameters (printing speed and pressure), the engraved cylinder cell parameters (tone, screen angle, line density and stylus angle), as well as by modifying the ink formulations [46–48]. There are several cell parameters related to the engraved cylinder surface pattern, which are cell volume, cell depth, wall width, channel width, tone, screen angle, line density and stylus angle [34]. Normally the latter four inter-related parameters are used to optimize the cell patterns. As the printing parameters need to suit the engraved plate designed for printing OPV modules, preliminary printing experiments should be conducted using different solution concentrations for the module fabrication. Line density is the main parameter for thickness control; the lower the line density, the larger the cell volume and the thicker the film. Some studies have shown that OPVs could be produced by laboratory-size gravure printers [23,24,46–48]. However, no study exists until now that the OPVs have been fully printed by a gravure process with a PCE over 2%.

Herein, it is reported for the first time the fabrication of fully gravure printed large-area OPV modules on flexible PET substrates with inverted architecture. The major challenge to overcome is the low adhesion between the subsequent layers, which leads to printing inhomogenities and current leakage in the final OPV devices. This can be done by properly adjusting the surface energy of the bottom layer, which has to be higher than the surface energy of the printed layer on top of the bottom layer [49,50]. An example could be when attempting to print the water-based PEDOT:PSS ink onto the low surface energy hydrophobic layer P3HT:PCBM or other active layers.

In this study, we have printed fully functional OPV modules by a sheet-to-sheet (S2S) lab-scale gravure printing process, with the same printing speed, drying temperature and drying time for each printed layer. This is of paramount importance and allows the direct transfer of the experimental protocol to a scalable, high throughput and production yield R2R gravure printing process for volume production of OPVs. This achievement could be realized that it enables the complete manufacturing of OPV modules in a single printing process using multiple printing and drying stations. This can increase the yield of the fabrication process and decrease dramatically the cost of OPV modules. Initially, several systematic experiments were performed in order to eliminate the interfacial tension of the OPV layers, by studying the substrate surface energy, surface tension of inks; and by controlling these factors, OPVs with optimum layer characteristics were achieved. More specifically, the inverted OPV modules have been prepared by successively printing the electron transport layer (ETL) on indium tin oxide (ITO) coated polyethylene terephthalate (PET), the active polymer layer, the hole transport layer (HTL) and finally the silver (Ag) top electrode. All the printing steps were performed in ambient atmosphere and optimized for each OPV layer to get the optimum printability. The total area of the OPV modules was 45 cm^2 and composed of 8 interconnected cells exhibiting a maximum power conversion efficiency (PCE) of 2.22%, short-circuit current (J_{sc}) 9.73 mA/cm^2, open-circuit voltage (V_{oc}) 4.3 V (0.54 V per cell) and fill factor (FF) of 43%. SEM and TEM studies demonstrated the pinhole free OPV devices and the morphological characteristics of the OPV multi-layer system. Spectroscopic Ellipsometry (SE) characterization has revealed the optical and electronic properties, the phase separation and the vertical distribution of the donor and acceptor components in the photoactive blend layer. The PCEs could be potentially improved by the further optimization of the layer thicknesses and the flexible PET/ITO substrate properties. The optimum printing parameters reported in this study can be directly transferred from the lab scale printing to an industrial scale roll-to-roll (R2R) manufacturing process.

2. Experimental

2.1. Materials and inks

Commercially available heat stabilized PET/ITO was used as the flexible substrate (thickness: 175 μm, sheet resistance: ~50 Ω/sq). A mixture of hydrochloric acid (HCl, 38%), distilled water (d-H_2O) and nitric acid (HNO_3, 65%) was used for the chemical etching of ITO. In order to remove any residuals after chemical etching, the substrates were dipped for 5 min in an ultrasonic bath of isopropanol, followed by absolute ethanol, acetone and water. Commercial zinc oxide (ZnO) ink consisted of nanosized ZnO particles was used for the electron transport layer (ETL). Poly(3-hexylthiophene) (P3HT, Advent) and [6,6]-phenyl C61 butyric acid methyl ester (PCBM, technical grade, 99.5%, Solenne BV) were blended to form the active layer (1:0.8 in o-DCB with a concentration of 160 mg/ml). An aqueous dispersion of poly-3,4-ethylenedioxy-thiophene:poly(styrene sulfonic acid) (PEDOT:PSS, Clevios™ CCP105, Heraeus) was used for the hole transport layer (HTL). Silver dispersion ink (Ag ink) with low sintering temperature from Sigma-Aldrich has been used as top contact. All the chemical reagents and inks were used as received without further purification or treatment.

2.2. OPV architecture and module fabrication

PET/ITO substrates (12 × 22 cm) were initially patterned with chemical etching, by covering with eight protecting vinyl tapes with a rectangular shape (4.0 × 0.7 cm) at fixed distances, and immersing the substrates for 30 s in a mixture of $HCl/H_2O/HNO_3$ (volumetric ratio of 10:10:1). Afterwards, the substrates were removed and cleaned several times with d-H_2O. The vinyl tapes were removed then and the ITO remaining areas were functioning as the bottom contacts for each of the OPV single cells. PET/ITO patterned substrates were exposed then to O_2 plasma activation/cleaning treatment for 5 min at a pressure of 1.2 mbar and at 40 W power of the plasma reactor. As a next step, ZnO nano-particle ink was printed by gravure at a speed of 18 m/min and dried on a hot plate at 140 °C for 1 min. A 16.0% w/v (160 mg/ml) P3HT:PCBM in ratio 1:0.8 solution was prepared in o-DCB the previous day and kept under stirring overnight at 80 °C in N_2 environment to dissolve completely the two blend components. Once the ZnO layer was dried, the P3HT:PCBM was printed also by gravure using the same printing speed of 18.0 m/min and the same drying time and temperature as well. The substrates were exposed finally to O_2 plasma for 20 s at a pressure of 1.12 mbar and at 10 W power, in order to create slightly some polar groups or radicals that allow the deposition of the PEDOT:PSS. The PEDOT:PSS solution and Ag ink were successively printed and dried with the exact same conditions as the previous two layers.

Fig. 1a shows a top schematic view of the OPV module geometry demonstrating its inverted architecture and indicating the connection of the Ag top electrode to the ITO bottom electrode of the next cell in the series connection. Fig. 1b shows the cross-sectional schematic of the module structure with 8 serially