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Flexible polymer solar cell modules with patterned vanadium suboxide layers deposited by an electro-spray printing method

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ABSTRACT

Vanadium suboxide (VO_x) layers deposited by an electro-spray (e-spray) printing method were applied to the fabrication of high efficiency patterned polymer solar cell (PSC) modules. By tailoring surface tension and the atomization condition of the e-sprayed sol precursor, e-sprayed VO_x layers on top of both hydrophilic and hydrophobic surfaces were successfully obtained, which enabled alternative architectures of conventional/inverted cells in a sub-module. The integrated PSC module that alternatively incorporated patterned metal oxide layer exhibited the high aperture power conversion efficiency (PCE) of 4.93% with a geometric fill factor (GFF) of 87%. Furthermore, we achieved the high aperture PCE of 4.72% on the flexible polyethylene terephthalate (PET) substrate comparable to that on the glass substrate which is applicable to large area roll-to-roll PSC module production.

1. Introduction

Polymer solar cells (PSCs) based on bulk heterojunction (BHJ) blends of conjugated polymers and fullerene derivatives have been considered a promising energy harvesting source due to their outstanding features of low-cost and high-throughput printing processes [1–3]. Recently, power conversion efficiencies (PCE)s over 10% were achieved in PSCs [4].

Despite such outstanding improvements in the performance of PSCs, however, there are still several issues to be resolved for their commercialization. One problem is the fact that those high PCEs have been achieved in lab-scale unit cells fabricated mostly by spin coating methods [5–7]. To realize meaningful high performance in PSC modules, each unit cell must be fabricated with a large-area using printing methods and the cells should be properly constructed to minimize the PCE drops in modular shape compared with the lab-scale small cells.

The slot-die coating technique is a promising fabrication method for depositing organic component layers (active layers and interlayers) on large-area PSC modules. In fact, until now, most reported PSC modules have been fabricated by this method, and therefore, these modules consist of several stripes of one-dimensional patterning with identical width, and these stripes are series-connected [8–10]. In this module architecture, blank shifts of each layer are implemented to avoid undesired coating and an interconnection area between the unit cells, resulting in low geometric fill factors (GFF: the ratio of the photoactive area to the total area) with large aperture loss. One might hypothesize that the GFF could be improved by increasing the width of the stripe pattern. However, because this approach causes a significant PCE drop due to ohmic loss originating from the relatively low conductivity of transparent electrodes, this is not an ideal solution for this issue [11,12]. Therefore, the PCE of large-area printed modules is still quite low compared with those of the lab-scale PSCs.

To minimize the gap between the unit cell PCE and the module PCE (by improving the module GFF), we developed an effective module architecture in our previous works [13,14]. The highly efficient PSC modules were constructed of alternating interlayers for manufacturing opposite charge polarity and were serially connected by seamless continual terminal (SELECT) electrodes. With our new module architecture, a GFF ~90% was achieved with the 4.24% module PCE, which corresponds to 82% of the lab scale PSC's PCE. Despite those remarkable achievements in the module's performance, however, the fabrication process of our module architecture has a significant drawback, as it requires a

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vacuum deposition process for the thin molybdenum oxide (MoO_3) interlayer. Because this process is not compatible with the roll-to-roll technique, this vacuum process should be replaced by a solution-based method to take advantage of printable PSC fabrication.

In this study, we developed an electro-spray (e-spray) method to coat thin vanadium suboxide (VO_x) films in our new PSC modules. Because the mist size of the e-spray ink is determined by the biased voltage during the e-spray deposition, we can easily control the drying time and thickness of the VO_x films [15,16]. Moreover, by manipulating the surface tension and atomization conditions of the e-sprayed VO_x solution (s-VO_x), we were able to deposit thin uniform VO_x layers on top of the hydrophobic photoactive layers as well as on the hydrophilic organic interfacial layers. As a consequence, we demonstrated efficient flexible PSC modules fabricated by all-solution processing.

2. Experimental

2.1. Materials

Electron donor material poly [N-9′′-hepta-decanyl-2, 7-cabazole-alt-5,5-(4′, 7′-di-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) and acceptor fullerene derivative [6,6]-phenyl C_{71}-butyric acid methyl ester ($PC_{71}BM$) were purchased from 1-material and Nano-C, respectively. Polyethyleneimine (PEI) (Aldrich 50 wt% in H_2O) was diluted in deionized water to 0.05 wt%. The sol–gel processed vanadium oxide precursor was prepared by dissolving 0.1 ml of vanadium isopropoxide (Aldrich) in 40 ml each of methanol, isopropyl alcohol, butanol, and pentanol under ambient conditions, respectively. Patterned ITO/glass and ITO/ polyethylene terephthalate (PET) substrates were first cleaned with detergent, then ultrasonicated in distilled water, acetone and isopropyl alcohol, and subsequently dried in an oven.

2.2. Device fabrication

For the fabrication of the PSC modules, a 0.05 wt% solution containing PEI in a mixed solvent was spin-cast at 5000 rpm for 30 s after waiting 15 s and was dried at 80 °C for 10 min in air. The first VO_x layer for the regular sub-cells was deposited onto the regular cell position of the substrates by the e-spray coating method through a shadow mask. The s-VO_x was loaded into a 5 mL syringe equipped with a 23-G sized metal nozzle. The distance between the solution-loaded tip and the substrate was maintained at 6 cm and the applied voltage was 5–7 kV with respect to the substrate and the metal shadow mask. The s-VO_x was injected using a syringe pump at a speed of 20 μm/min. The e-spray process was performed at a substrate temperature of 50 °C and a humidity of 40% in ambient air conditions. After deposition, the layer was dried at 80 °C on a hotplate for 5 min. Then, a 0.4 wt % solution containing a mixture of PCDTBT:$PC_{71}BM$ (1:4) in dichlorobenzene was spin-cast on top of the underlying VO_x and PEI layers, followed by annealing at 80 °C for 30 min under N_2 to form a thin film with a thickness of approximately 80 nm. E-sprayed VO_x films were deposited on top of the inverted region under the same conditions for VO_x film deposition for the regular structure. The solar cell modules were completed by evaporating aluminum (Al) electrodes through a shadow mask in high vacuum (10^{-6} mbar). In the case of the spin cast VO_x layer, VO_x solution was spin-cast at 3000 rpm for 40 s and at 2000 rpm for 40 s after waiting for 20 s, then dried at 80 °C for 10 min in air.

2.3. Measurements

Current density–voltage (J–V) characteristics of the unit cells and the modules were measured using an Iviumstar high power electro chemical analyzer Source Measure Unit under Air Mass 1.5 Global (AM 1.5 G) simulated solar illumination at 100 mW cm^{-2} from an Abet Technologies Sun 3000 solar simulator. The incident-photon-to-current-efficiency (IPCE) measurements for the conventional and inverted PSCs were performed with a Solar Cell Spectral Response/ QE/IPCE measuring system. Scanning electron microscope (SEM) images were taken with a Hitachi S-4700 instrument. For transmission electron microscopy (TEM) measurements, a thin section of the device was obtained by a focused ion beam technique. Cross-sectional images of the samples were characterized by TEM analysis instrumentation operated at 300 kV.

3. Results and discussion

Fig. 1(a) illustrates a schematic of the module fabrication concept using e-spray coating for the VO_x functional interlayers for our SELECT module. Our new module consists of alternating regular and inverted sub-cells that are serially connected by sharing the top and/or bottom electrodes between the neighboring sub-cells, as described in detail in our previous publications [13,14].There are several advantages to our SELECT module architecture, such as printing active layers in large-areas without any patterning, avoiding any electrical short problems arising from misalignment of the top electrodes, and minimizing aperture losses with the blank offset coating. These advantages originate mainly from the absence of direct electrical connections between the top and bottom electrodes of the subsequent sub-cells in our SELECT module.

We fabricated our modules using a bulk heterojunction (BHJ) composite PCDTBT and a fullerene derivative, $PC_{71}BM$, as a photoactive layer; PEI as an electron transport layer (ETL); and VO_x as an hole transport layer (HTL) (Fig. 1(b)) [17–20,25]. In our module, regular and the inverted sub-cells are determined by the position of the VO_x layers. When the VO_x layer is placed on top of the BHJ (PCDTBT:$PC_{71}BM$) layer, the parts behave as inverted subcells, whereas the regular sub-cell parts place the VO_x layer between the BHJ and the PEI layers. Thus, the regular and inverted sub-cell structures are ITO/PEI/VO_x/PCDTBT:$PC_{71}BM$/Al and ITO/PEI/PCDTBT:$PC_{71}BM$/VO_x/Al, respectively. It is notable that the PEI/VO_x double layer acts as the HTL in the regular subcells. Although PEI is an excellent work-function (WF) modifying material and is used as the symmetry-breaking ETL for the inverted cells, the WF shift of ITO by PEI in the ITO/PEI/VO_x combination layers of the regular cells does not influence device's performance. Therefore, the photo charge carriers generated in the photoactive layer move to the correct electrodes for each sub-cell, as described in Fig. 1 (c) and (d).

The essence of our SELECT module architecture is to place patterned VO_x films on the PEI and BHJ layers. In contrast with our previous works that used a vacuum deposition process for the MoO_3 layers, we used an e-spray method to form patterned VO_x films in this work. Vanadium isopropoxide dissolved in isopropyl alcohol (i-VO_x) was pumped into the metal nozzle with a syringe pump to form drops at the apex. A sufficiently high voltage was applied to the metal nozzle, and the electric field induced by this high voltage forced the i-VO_x solution to be jetted and broken into highly charged liquid drops of small size. These charged drops (or fine mist) were radially dispersed by Coulomb repulsion and guided by the electric field to the target substrate via a shadow mask, as schematically shown in Fig. 1(a). In addition, the atomization condition determining the size and distribution of