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Organic solar cells all made by blade and slot–die coating techniques

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ABSTRACT

In this work, polymeric solar cells with the configuration anode/Hole Transport Layer (HTL)/Active Layer/Cathode, with an active area of 3 cm^2 were fabricated layer by layer, including the cathode, by doctor blade and slot–die techniques at normal room atmosphere and temperatures about 90 °C for cathode deposition. Further, small modules were built on a single substrate with 3 cells connected in series (active area of 9 cm^2). The best electrical parameters for single cells were open circuit voltage (V_{oc}) = 571 mV, short circuit current density (J_{sc}) = 7.69 mA/cm^2, fill factor (FF) = 0.55, and power conversion efficiency (PCE) = 2.4%, meanwhile for modules V_{oc} = 1.54 V, J_{sc} = 2.09 mA/cm^2, FF = 0.55, and PCE = 2.1%. The main parameters of the deposition technique such as substrate temperature, blade speed and bar–substrate gap were evaluated to ensure the best photovoltaic (PV) device performance. For the active layer, a co–solvent system based on chloroform and 1,8 diiodoctane was used to dissolve the blend poly(3–hex ilthiophene–2,5dyil): [6,6]–Phenyl–C71–butyric acid methyl ester (P3HT:$PC_{71}BM$). The utilized cathode, named Field's metal, was an eutectic alloy of Bi:In:Sn (32.5:51:16.5%) with a melting point about 65 °C; thus, this metal is easily melted and deposited by blading process on the active area. The obtained PV parameters demonstrate high viability of the bar coating process both for the fabrication of solar cells and small solar modules.

1. Introduction

During the last years, polymeric solar cells (PSCs) with efficiencies over 10% have been reported (Kang et al., 2016; Green et al., 2015; Polman et al., 2016). Such efficiencies are usually obtained for devices with very small area, fabricated under inert laboratory atmosphere and by using evaporated cathodes under high vacuum conditions. In order to develop high throughput fabrication processes, several approaches should be explored to fabricate devices with medium and large area under ambient conditions, while preserving acceptable power conversion efficiency. Besides screen printing, the usual methods for deposition of organic layers over large areas are blade or slot–die coating techniques that have been used not only for PSCs (Liu et al., 2015; Jin et al., 2012; Lim et al., 2012; Hong et al., 2013; Krebs, 2009) but also organic light emitting diodes and perovskite solar cells devices (Choi et al., 2015; Deng et al., 2015). However, for the typical device architecture ITO/Hole Transport Layer/Active Layer/Electron Transport Layer/Cathode, only the hole transport and the active layer are usually deposited by blade techniques (Lim et al., 2012; Krebs, 2009), while spin coating or evaporation is used for deposition of the electron transport layer and cathode. For instance, Lim et al. (2012) reported photovoltaic cells based on the polymer POD2T–DTBT with an efficiency of 6.49%, where the PEDOT:PSS layer was deposited by spin coating in order to obtain a thickness of about 40 nm, while the active layer was deposited by doctor blade at normal room atmosphere. In this case devices were fabricated without any electron transport layer and, aluminum was evaporated as cathode. Because the thickness for PEDOT:PSS must range between 30 and 50 nm, homogeneity over large areas is required. Concerning these problems, Tsai et al. (2015) pointed out that owing to the depleting of solution, the thickness of PEDOT:PSS films deposited by doctor blade decreases along the coating direction leading to a non–uniformity layer. They reported that a second round of coat-

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ing in the reversed direction was necessary to obtain a homogeneous film with a thickness about 36 nm over an area of 12 × 15 cm. However, this second deposition was not suitable for the active layer (P3HT:$PC_{61}BM$) because there was a poor contact between the deposited films, which leads to a decrease in the fill factor and thus, the PV performance was also affected. Here, devices were completed with the evaporation of LiF and Al as electron transport layer and cathode respectively and, an efficiency of 3.65% was reported.

For doctor blade or slot–die coating techniques, it is possible to have control of thickness and morphology of the active layer by taking care of several parameters; some of the crucial ones are: the used solvent to dissolve the donor polymer and the fullerene acceptor, the gap between blade and substrate, the speed of blading, the plate temperature and the conditions during the drying process (Liu et al., 2015; Lim et al., 2012 and Hong et al., 2014). Solvents for spin coating deposition are also used for blade technique; however, in the latter method temperature is elevated for drying solution during deposition. For blade or slot–die coating techniques the evaporation rate of the used solvent determine some characteristics of the deposited film, i.e., the thickness, the morphology and the adequate phase morphology between the polymer and fullerene. For an active layer based on P3HT:$PC_{61}BM$, Hong et al. (2014) reported the use of chlorobenzene (CB) or dichlorobenzene (DCB) as well as a mixture of them (co–solvent system) as solvent. To obtain the desired thickness they fixed the plate temperature (80 °C), the blade–substrate gap (50 μm) and varied the coating speed between 0.5 and 1.0 m/min. The main observed effect was due to the used solvent; a more uniform and crystallized morphology was reported with the co–solvent system owing to a better mixture and slower drying process, also a more homogeneous surface was observed. The *PCE* achieved with CB, DCB and CB–CDB system was 2.7%, 2.4% and 3.1%, respectively, for cells with an active area of 1 cm^2. For this report both, the active layer and the hole transport layer (PEDOT:PSS) were deposited by doctor blade while evaporated aluminum was used as cathode.

On the other hand, solvents with high vapor pressure are not usually considered for blade coating techniques because their fast evaporation leads to non–uniform morphology. For active films deposited by slot–die coating, Liu et al. (2015) reported the use of chloroform with DCB as additive and achieve a good blend of the bulk–heterojunction layer based on the copolymer of diketopyrrolopyrrole and quaterthiophene blended with PCBM. Morphology was controlled by the volume of DCB showing an influence on the final performance of devices due to crystallization and phase segregation; with 5% of DCB, the V_{oc}, J_{sc}, *FF* and *PCE* were 650 mV, 14 mA/cm^2, 0.57 and 5.5%, respectively. In the latter work, LiF was used as the electron transport layer and aluminum as the cathode; both of them were evaporated under high vacuum conditions.

In this work the fabrication of organic solar cells and modules is reported where the hole transport layer, active layer and also the cathode were deposited by blade or adapted slot–die coating techniques. A doctor blade equipment with a modified applier to use it as slot–die coater was employed. Typical parameters such as plate temperature, gap between applier and substrate as well as deposition speed were explored to obtain a homogenous film of PEDOT:PSS as well as P3HT:$PC_{71}BM$ blend. The cathode was an eutectic alloy of three metals: Bi, 32.5%; In, 51% Sn, 16.5% known as Field's metal (FM) deposited at about 90 °C under regular atmosphere. FM and a similar eutectic alloy have been described previously by our research group as an effective and low cost cathode for PSCs (Nolasco et al., 2014; Salinas et al., 2011; Pérez-Gutiérrez et al., 2014; Romero-Borja et al., 2015; Álvarez-Fernández et al., 2016). Eutectic alloys are attractive because they provide an easy and fast way for fabricating top–metal electrodes since they melt at low temperatures (below 100 °C), and allow deposition under a normal atmosphere, thus avoiding vacuum processes. Moreover, the material and deposition cost is significantly low compared with that for traditional metals and their implementation by high vacuum evaporation procedure. However, it is also true that some eutectic alloy deterioration could take place in real applications because devices must tolerate temperatures up to 65 °C. Other eutectic alloys with melting point about 140 °C, such as that one composed by Bi and Sn (58% and 42%, respectively), could be used to avoid any inconvenience with sun light heating under real conditions; tests of this alloy for the top electrode implementation on OPVs devices are currently taking place in our group.

The best PV parameters obtained for 3 cm^2 cells were V_{oc} = 571 mV, J_{sc} = 7.69 mA/cm^2, *FF* = 0.55 and *PCE* = 2.4%, while for modules (three single cells connected in series) were V_{oc} = 1.54 V, J_{sc} = 2.09 mA/cm^2, *FF* = 0.55 and *PCE* = 2.1%.

2. Experimental section

2.1. Materials

ITO/glass substrates with 5–15 Ω/square were acquired from Delta Technologies. Polymer P3HT and the electron acceptor PC_{71}-BM were purchased from Rieke metals and American Dye Source, Inc., respectively. PEDOT:PSS (Clevios PVP AI4083) was obtained from Heraeus–Clevios. All solvents were acquired from Sigma Aldrich and used as received; Field's metal was acquired from Rotometals.

2.2. Device fabrication

ITO/glass substrates (5 × 5 cm) were patterned to have three cells by substrate, then they were cleaned with ethanol in an ultrasonic bath and rubbed with alcohol wetted cotton. After this procedure, substrates were dried with clean and dry air and kept at 85 °C over 12 h. Before deposition of the polymer layers, the substrates were treated with UV oxygen plasma for 5 min. PEDOT:PSS was diluted with 20% v/v of distilled water and then blade coated onto ITO, to coat a 5 × 5 cm^2 substrate 300 μl of diluted PEDOT:PSS were used. For this layer the temperature of doctor blade plate was set at 95 °C and the gap between blade and substrates as well as the coating speed were varied in order to analyze their effect on the thickness; the gap was set by means of feeler gauges. The PEDOT:PSS layer was annealed at 85 °C for 15 min in air. For the active layer, a solution of P3HT:$PC_{71}BM$ (1:0.8 wt%) with a concentration of 19 mg/mL was prepared with chloroform–DIO (1:0.04 v/v%) as solvent. The active layer was slot–die coated onto PEDOT:PSS film; for this case, the machine plate was set at room temperature and also the gap between blade and substrates as well as speed of coating were varied to get the proper thickness. After deposition, samples were annealed at 85 °C in air during 15 min.

The active layer was masked according to the substrate pattern to carry out the cathode deposition (active area of 1 × 3 cm^2 for a single cell), as well as the series connection (3 cells per substrate). Then the substrates were placed on the plate of doctor blade equipment and heated at 90 °C. The melted metal (previously heated at the same temperature) was dropped at the beginning of the substrate and blade–coated over the entire mentioned area, the gap between the blade and substrate was of 0.04 mm, the speed of coating was 10 mm/s. The obtained metal layer had a thickness of 0.25 mm because the liquid metal shows a redistribution after the blading process. Finally, device was removed from the blade plate and cooled down to room temperature. Fig. 1a shows a dia-