Solar Energy Materials & Solar Cells 137 (2015) 44–49

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

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

Enhanced stability in semi-transparent PTB7/PC71BM photovoltaic cells

Pablo Romero-Gomez [a,*], Rafael Betancur [a], Alberto Martinez-Otero [a], Xavier Elias [a], Marina Mariano [a], Beatriz Romero [b], Belén Arredondo [b], Ricardo Vergaz [c], Jordi Martorell [a,d]

[a] ICFO-Institut de CienciesFotoniques, Mediterranean Technology Park, 08860 Castelldefels, Barcelona, Spain
[b] Escuela de Ciencias Experimentales y Tecnología, Universidad Rey Juan Carlos, 28933 Móstoles, Madrid, Spain
[c] Escuela Politécnica Superior, Universidad Carlos III de Madrid, 28911 Leganés, Madrid, Spain
[d] Departament de Fisica i Enginyeria Nuclear, Universitat Politècnica de Catalunya, Terrassa, Spain

ARTICLE INFO

Article history:
Received 5 September 2014
Received in revised form
1 January 2015
Accepted 18 January 2015
Available online 7 February 2015

Keywords:
PTB7
OSC
Stability
Warburg
Inverted
Photonic crystal

ABSTRACT

We studied the performance over time of opaque and semi-transparent PTB7:PC71BM bulk heterojunction solar cells. For unsealed inverted configuration cells we observe that when the isolation from the environment is improved, the degradation observed is dominated by one single exponential decay. We demonstrate that a dielectric multilayer stack of approximately 550 nm provides an isolation that increases the lifetime of the cell close to ten times. In that event the fill factor appears to be the PV parameter dominating cell degradation resulting from a decrease in the shunt resistance. An Impedance analysis we performed indicates that a Warburg element, attributed to the presence of slowly moving charges such as heavy ions, must be included in the description of the experimental data. The contribution from such element increases as the cell degrades in good agreement with a degradation dominated by the corrosive effects from external agents reaching the active layer of the device.

1. Introduction

Since the early works on organic solar cells (OSC), many different polymers have been synthesized towards the goal of obtaining an active material with an optimal photon to charge conversion that would make such type of cells a commercially viable technology. In recent years, cells made with bulk hetero-junctions (BHJ) of PTB7/$PC_{71}BM$ have emerged as one of the most promising polymer based devices combining the unique features of an organic based technology with a relatively high power conversion efficiency (PCE) [1,2]. Interestingly, it has been shown that such polymer blend can be used to obtain high performance homogenously semi-transparent solar cells [3]. Unlike semi-transparent cells fabricated using other types of polymers or PV technologies, with PTB7 one may fabricate devices which do not alter the colour of the objects seen through them. However, despite the high PCEs obtained and the potential for the PTB7/$PC_{71}BM$ blend to be used in building integrated PV, any practical application for such cells would be pending on the final stability of the devices fabricated using such blend.

For many different kinds of organic based PV cells it has been reported that the penetration of oxygen and moisture into the active layer of the cell results in severe loss of performance [4–8]. In the standard OPV configuration, the acidic nature of the poly(3,4-ethylenedioxylenethiophene):poly(styrenesulphonic acid) (PEDOT:PSS) used as electron blocking layer (EBL) [9,10] leads the etching of the indium tin oxide (ITO) electrode [11]. For instance, in P3HT oxygen has been demonstrated to react with the side chain by insertion in the alpha position relative to the thiophene ring [12]. In polyfluorenes oxygen insertion next to the quaternary carbon leads to fluorenone units and results in severe damage of the polymer properties [13]. Blocking of similar carbon positions with bulky side chains that prevent oxygen insertion has resulted in important increases in device stability [14], especially when aryl groups are used instead of alkyl chains. Large improvements in the stability of organic devices can be obtained in inverted configurations that bypass the need to use PEDOT:PSS. In such architecture, n-type metal oxides such as ZnO or TiO_2 are deposited on the ITO layer to lower the work function of the electrode [15,16], while NiO, WO_3 or MoO_3 may be used as EBL [11]. Further improvements in stability may be reached by an adequate isolation from the most aggressive external agents [4].

In the current work we study the stability of cells which use PTB7:PC71BM as the active blend. In particular we show that the

* Corresponding author.
E-mail address: pablo.romero@icfo.es (P. Romero-Gomez).

http://dx.doi.org/10.1016/j.solmat.2015.01.026
0927-0248/

incorporation of a 1-D multilayer structure combining three layers of high refractive index (HRI) and two layers of low refractive index (LRI) dielectric materials to enhance the efficiency of semi-transparent cells [3] acts also as an efficient barrier to protect the cell from a rapid degradation. In the first part of the work, a comparison between the stability of opaque and semi-transparent cells is provided. In the second, the performance of opaque and semi-transparent inverted devices is compared, and the impact of the multilayer structure (ML) over the long term stability is analysed.

2. Experimental

2.1. Device fabrication

To fabricate the photovoltaic devices we used 120 nm thick ITO-patterned substrates. For the standard configuration, PEDOT:PSS was used as EBL while thermally evaporated BCP as HBL. Details of the preparation of such cells can be found elsewhere [17]. For the inverted solar cells, a thermally evaporated MoO_3 layer was used as EBL while ZnO was used as HBL. The ZnO layer was grown by sol–gel where the precursor solution was prepared according to Ref [18]. Spin coating was performed at 6000 rpm during 60 s followed by a thermal annealing at 200 °C during 20 min in air. In the semi-transparent devices, a 10 nm thick silver back electrode was thermally evaporated at 5.5 Å s^{-1} onto a substrate cooled down to −5 °C [19]. The thicknesses for all the layers are reported in Table 1 (note that all devices have the same active layer thickness). We fabricated five different types of non-encapsulated PTB7:$PC_{71}BM$ BHJ cell architectures (see Fig. 1): Standard opaque (Std-Opaque), Standard semi-transparent (Std-ST), inverted opaque (Inv-Opaque), inverted semi-transparent (Inv-ST), and inverted semi-transparent with a multilayer trapping structure (Inv-ML-ST). Thicknesses of the photovoltaic cell layers were determined numerically to optimize light harvesting in the opaque configuration [3,17,20] with the only constraints imposed by the fabrication procedures or the charge collection limitations of the materials used. The photovoltaic part and the photonic structure deposited on top of the transparent Ag electrode may be clearly distinguished in the field-emission scanning electron microscopy (FESEM) cross-section view of the Inv-ML-ST device shown in Fig. 2.

In order to make Std-ST, Inv-ST, and Inv-ML-ST devices semi-transparent, the back silver contact was made 10 times thinner than for the opaque cells (i.e. 10 nm instead of 100 nm thickness). Std-ST and Inv-ST devices where capped with a 10 nm protective MoO_3 layer deposited on top of the back Ag contact. For the Inv-ML-ST device, such protective layer was replaced by the photonic crystal, a five-layer structure based on MoO_3 (HRI) and MgF_2 (LRI). The structure was designed numerically to provide the adequate light management to optimize the performance of the cell, i.e. to increase light trapping in the near IR and near UV region. Details on such numerically based optical optimization for semi-transparent cells can be found in Ref. [3], where a similar analysis was applied to optimize the PCE of semi-transparent standard cells.

Table 1
Thicknesses (in nm) for all layers in the five different configurations considered.

	ITO	PEDOT:PSS	ZnO	BHJ	BCP	MoO_3	Ag	MoO_3/MgF_2
Std-Opaque	120	40	–	100	3.5	–	100	–
Std-ST	120	40	–	100	3.5	–	10	10/0/0/0/0
Inv-Opaque	120	–	30	100	–	5	100	–
Inv-ST	120	–	30	100	–	5	10	10/0/0/0/0
Inv-ML-ST	120	–	30	100	–	5	10	112/136/102/102/102

2.2. Device characterization

The PCE of the fabricated devices was determined from current density–voltage curve measurements obtained under 1 sun, AM 1.5G spectrum illumination from a solar simulator (Abet Technologies, model Sun 3000). The solar simulator illumination intensity was monitored using a monocrystal silicon reference cell (Rera Systems) calibrated against a National Renewable Energy Laboratory calibrated reference cell. In the characterization of all semi-transparent cells, illumination was from the ITO side. Impedance spectroscopy (IS) measurements were performed under illumination conditions using a standard red LED. A Solartron 1260 impedance analyzer was used (Solartron Analytical, Farnborough, UK). The cell was connected to the analyzer that fed the input signal, biasing the device at different dc levels and superimposing an alternating signal with amplitude 100 mV and sweeping frequency from 1 Hz to 1 MHz.

3. Results and discussion

3.1. Time evolution of the PV parameters

The study the aging process of the fabricated devices was performed according to the ISOS-standards defined in Ref. [21]. We performed two sets of experiments. In one set we compared the performance of the Std-Opaque and Std-ST configurations relative to the Inv-Opaque one, while in a second set we compared the three different inverted configurations. The PV parameters for each cell were measured at the start of the aging process (cf. Table 2). All PV parameters measured subsequently were normalized to the corresponding initial values. In between measurements the cells were stored at ambient conditions in the dark, which corresponds to ISOS-D-1 shelf test at level 2 according to consensus stability testing protocols for OPVs [21]. With such level 2 test we aimed at determining the role played by the ML on the lifetime of the cells and determine the origin of cell degradation under such conditions. In our study, the cell lifetime is taken as the time the cell efficiency drops to 80% of its initial value [21].

The time evolution of the main PV parameters (V_{oc}, J_{sc}, FF and PCE) for the first set of time evolution experiments is shown in Fig. 3. As it has been reported with other polymer blends, the acidic nature of the PEDOT:PSS in contact with the ITO causes a rapid degradation of the FF and V_{oc} [22]. Such source of rapid degradation may mask any other source of degradation possibly related to the thickness of the capping metal electrodes and consequently we observe that Std-Opaque and Std-ST degrade at a very similar speed. On the contrary, the Inv-ST cells exhibit a lifetime of approximately 250 h, corresponding to at least 50 times the lifetime of the other two cells.

In the second set of experiments we considered only the inverse configurations. The evolution of all PV parameters for the three cells under study is shown in Fig. 4. As in the previous set of time evolution experiments the cells were stored in air and under darkness in between measurements. For all three inverted cells, the FF exhibits a degradation faster than V_{oc} and J_{sc}. Consequently the efficiency followed, to a large extent, the evolution of the FF. Note that the lifetime for the Inv-Opaque with a capping electrode of 100 nm is 800 h, close to three times the lifetime of the Inv-ST which is only capped with 10 nm of Ag and 10 nm of MoO_3. This suggests that external agents are a dominant source of degradation for the inverted cells and that thicker capping layer provide a better isolation from such agents. Note that for the Inv-ST and the Inv-Opaque a sudden drop in FF begins after 50 h and after 500 h, respectively. In the 3500 h of the study, this drop was not observed for the ML-ST cell.

To gain further insight in the degradation mechanisms of the latter device, the natural logarithm of the normalized FFs are shown in Fig. 5a for the three inverted devices. We observe that