

Optimization the lifetime of organic solar cells through optimization of the buffer layer

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ABSTRACT

The role of buffer layer inserted between active layer and Al contact in photovoltaic cells based on copper-phthalocyanine (CuPc) and C₆₀ was investigated is to optimise the lifetime of organic solar cells. The shelf life of un-encapsulated small-molecule organic solar cells, indium–tin oxide (ITO - anode)/copper phthalocyanine (CuPc - donor)/fullerene (C₆₀ - acceptor)/Buffer Layer/Al (cathode), have been studied under 100 mW/cm² continuous illumination in open air with different thin buffer layers of bathocuproine (BCP) and tris-8-hydroxy-quinolino-aluminum (Alq3). We studied the photovoltaic performances, including short circuit current density (J_{sc}), open circuit voltage (V_{oc}), power conversion efficiency (η_e) and fill factor (FF) of organic solar cells. We changed the thickness of the buffer layer (Alq3) to improve the effect of this layer on the life time of organic solar cells. In all cases two ageing mechanisms with two different time constants have been demonstrated and attributed to a rapid degradation of cathode contact followed by contamination of the active layer.

Keywords: Organic solar cell, Lifetime, Buffer layer, Degradation, Alq3.

1. INTRODUCTION

Due to a growing interest in organic semiconductor based devices in general [1, 2] and the need for renewable energy in particular [3], organic solar cells have been the object of increasing development during the last decade [4, 5]. Organic photovoltaic (OPV) cells have potential advantages over their inorganic counterparts of light weight and low-cost [6]. Unfortunately, the power conversion efficiency (η_e) [7 – 15] and lifetime [16 – 21] of OPV cells are far from satisfactory. For the cells based on copper phthalocyanine (CuPc)/fullerene (C₆₀) heterojunction structures, a very likely reason for their degradation is the decrease of conductivity of C₆₀ upon permeation [16, 20, 22]. Recently, the best efficiency of organic solar cells with bathocuproine (BCP) organic buffer has reached 5.7%, which shows a great potential for commercial applications [16, 23]. However the lifetime of organic solar cells with BCP buffer is unsatisfactory. In air and without encapsulation it takes only 20 min for the efficiency of the cells to decrease to half the initial value [24].

A small-molecule OPV cell with the structure ITO/donor(CuPc)/acceptor(C₆₀)/buffer layer/Al, lifetime improvement results probably from the reduced permeability of oxygen and moisture into the active layer due to the buffer layer such as BCP and tris-8-hydroxy-quinolino-aluminum (Alq3). In addition, the buffer layer blocks the diffusion of cathode atoms into the active layer during deposition. We found that the incorporation of BCP buffer, for example, accelerates degradation of the current and consequently the shelf life of the cells, due to crystallization of BCP, as demonstrated by polarised light microscopy. However, it was shown that performance of these cells improves when TPBI is used as a buffer [25].

In the this paper, performance of un-encapsulated cells with the structure ITO(100nm)/PEDOT-PSS(30nm)/CuPc(25nm)/C₆₀(40nm)/Alq3(Xnm)/Al(100nm), and an active layer surface of 25 mm², is discussed. We discuss cell optimization by varying the thickness of the buffer layer. Five similar organic solar cells were evaluated; with different thickness of Alq3 from 0 nm to 10 nm, measured in air under illumination using AM1.5 solar simulator (100mw/cm²).

2. EXPERIMENTAL

CuPc/C₆₀ cells are fabricated on pre-cleaned glass substrates coated with ITO anode with a sheet resistance of 20 Ω/square. Thin ITO layers were obtained by ion beam sputtering (IBS) using a target made up of a mixture of In₂O₃ and SnO₂ (90% and 10% by weight respectively). The targets were bombarded by argon ions accelerated at 6 keV with a current density of 1mA/cm² [26] at a pressure of 5.10⁻⁶ mbar. Active layers of CuPc-C₆₀-based cells were prepared as follows: A 30nm-thick layer of PEDOT-PSS, (Baytron PH from H.C. Starck) was deposited on the anode by spin coating, acting as a hole transport layer and as a barrier layer to prevent oxygen diffusion from ITO into the active layer [27, 28].

CuPc (Aldrich), fullerene C₆₀ (MER Corp., USA), BCP, Alq3, TPBI and lithium fluoride (LiF) (Aldrich), used as an exciton blocking layer (2.5nm) [29] prior to deposition of the aluminum cathode, were used without further purification. The consecutive vacuum sublimation of CuPc and C₆₀ was performed using a co-evaporation setup (by Joule effect) [30] built in house. The temperature of 3 cells dedicated to sublimation of organic molecules was monitored by a Eurotherm 2700 process regulator which allows a minimum growth rate, according to the quartz monitor sensitivity of 0.5Ås⁻¹. Vacuum sublimation was operated at a pressure of 10⁻⁶ mbar, and for all the experiments of this study, the growth rates were kept at 0.08nm/s and 0.1nm/s for CuPc and C₆₀ respectively. The aluminum cathode was deposited in an in situ confined bench, through a shadow mask delimiting a 0.25cm² diode area. Illumination was done using an AM1.5G solar simulator calibrated for 100 mW/cm².

3. RESULTS AND DISCUSSION

A. Using ALQ3

Figure I and Table II show the I-V characteristics of cells with the structure ITO/PEDOT-PSS(30nm)/ CuPc(25nm)/ C₆₀(40nm)/ Alq3(Xnm)/ Al(100nm), having different buffer layer thickness (X) showed in table I with the same illumination conditions.

Table 1: Different thickness of buffer layer (X nm) of different device

Device	Thickness of Alq3 (nm)
A	0
B	2.5
C	6
D	8
E	10

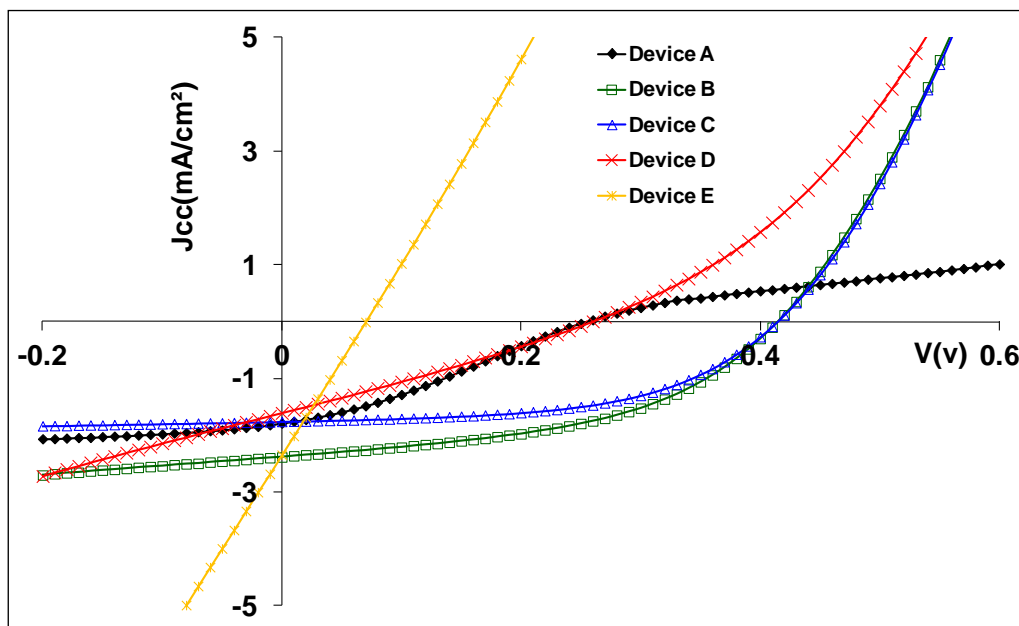


Figure 1: Comparison of the I-V characteristics of cells A, B, C, D and E (ITO/PEDOT-PSS(30nm) /CuPc(25nm) /C₆₀(40nm) /Alq3(Xnm) /Al, with X = 0 nm, 2.5 nm, 6 nm, 8 nm and 10 nm).

Table 2: Photovoltaic parameters for the various organic solar cells extracted from J-V characteristics of Figure. 4 under illumination.

Cell No.	η_e (%)	FF	Voc (V)	Jsc (mA/cm ²)
A	0.143	0.2924	0.26	1.787
B	0.48477	0.46012	0.42	2.3831
C	0.41237	0.53057	0.42	1.758
D	0.36202	0.2745	0.26	1.6063
E	0.04287	0.2172	0.08	2.4397

As indicated by our results, the buffer layer in all cells contributes to their stability relative to the buffer-free cell A, and that the photovoltaic parameters for all cells degrade when the buffer layer thickness increases [31].

Degradation of η_e for cells B, C and D is shown in Figure 2. All measurements were carried out in air without encapsulation. For example, as shown in the inset, η_e of cell B, where thickness of Alq3 layer is 2.5 nm, decreases to approximately 50% in 80 min. As the buffer layer thickness increases (cells C and D), the decrease in efficiency is not as significant over the same time range. If lifetime is defined as the degradation time of η_e from η_{e0} (η_{e0} it's the initial efficiency value at time = 0) to half of its original value, the lifetime for cells B, C and D can be estimated from Figure 2 at 80, 45 and 300 minutes respectively.

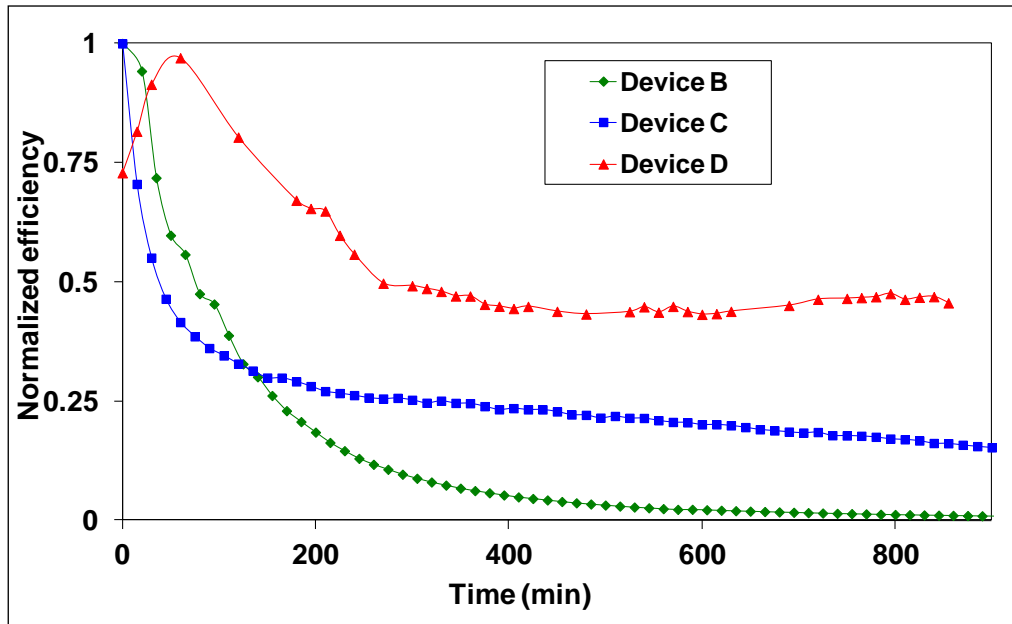


Figure 2: Normalized power conversion efficiency versus time for cells B, C and D (ITO/PEDOT-PSS(30nm) /CuPc(25nm) /C₆₀(40nm) /Alq3(Xnm) /Al, with X = 2.5 nm, 6 nm and 8 nm. Lifetime of all cells is measured in air.

In the case of cell B, the J(V) characteristics (Figure. 2.) decrease rapidly with time, causes by the degradation of the active layer, due to the thin buffer layer (Alq3 = 2.5 nm). In a first stage, there is a sharp decrease in efficiency, followed by a slower, nonetheless ongoing degradation in a second stage, while the other two cells, C and D, the second degradation stage is almost inexistent with the efficiency being constant with time. For cell D, J (V) characteristics degrade at a slower rate over time. Therefore, increasing the thickness of the buffer layer improves the lifetime but decreases the cell performance. After 855 minutes the efficiencies are 0.01%, 0.16% and 0.455% for Devices B, C and D respectively.

In general, organic solar cell degradation is first due to the degradation of the buffer layer. In the presence of moisture, this layer crystallizes, creating free space that facilitates the diffusion of O₂ and H₂O molecules towards the C₆₀ layer. It was shown that conductivity of the C₆₀ layer decreases by several orders of magnitude when exposed to oxygen, rendering it practically insulating, thus increasing drastically the series resistance and which results into poor J (V) characteristic [17, 31].

B. Discussion

For organic solar cells based on CuPc/C₆₀, one of the most important factors responsible for lifetime reduction is the permeation of oxygen into C₆₀. In the conventional structure of ITO/PEDOT-PSS/CuPc/C₆₀/Buffer layer/Al, after permeation through the thin buffer layer, oxygen diffuses into C₆₀ first, then into CuPc.

JSC decreases monotonously, which might indicate that other factors are responsible for the decrease of JSC in addition to the effect of oxygen and moisture. Figure 2 shows that while JSC of cell A is constant with time where only the cathode undergoes degradation, JSC of cell B decreases significantly due to the poor C₆₀/CuPc interface which resulted from the diffusion of oxygen and moisture into the active layer as assumed from the reduced conductivity of C₆₀. Such diffusion is limited when the proper thickness of the buffer layer is used, as is demonstrated in the behaviour of cell D in Figure. 2.

Further improvement in stability is obtained in the case of Alq₃ as analyzed below. As mentioned above, the crystallization of BCP is detrimental to the performance of organic solar cells because it results in a poor interface within the active layer caused by channels formed by oxygen and moisture penetration. However, the behaviour of cell D indicates that penetration of oxygen and moisture is lessened when Alq₃ is used, which was shown not to crystallize in air as is the case for BCP, as was demonstrated by polarized light microscopy. As a result, electrons from the dissociated excitons can pass through Alq₃ more easily due to the absence of gaps, and thus lead to an improved shelf life to more than 240 min for cell D. Though Alq₃ is more stable, oxygen can still penetrate into the C₆₀ layer after its penetration through Al and Alq₃ buffer resulting in an irreversible decrease of conductivity of C₆₀. This result indicates that Alq₃ is a more effective buffer than either BCP.

4. CONCLUSION

The performance of the C₆₀ layer in CuPc/C₆₀-based organic solar cells is very sensitive to the presence of oxygen/moisture. Deep electron traps created by such contaminants would reduce the electron mobility. Exciton dissociation takes place mainly at the interface between the fullerene and CuPc layers, and consequently, carrier collection depends on the conductivity of the organic films. The decreased performance observed upon ageing of the cells in the two different environments of our experiments means that conductivity of C₆₀ is dominant cause for degradation when the cell is operated in air. We have also shown that stability of the buffer layer when the cell is being operated affects the stability of the cell, and that of the three buffers, Alq₃ seems to result in more stable devices. As this buffer layer has a dual role of blocking diffusion of Al into the active layer during cathode deposition and minimizing diffusion of oxygen and moisture, its thickness and morphology are important parameters to consider when fabricating this type of cell. Increasing the buffer layer thickness is beneficial for limiting diffusion, but could backfire in terms of cell performance. Therefore, a compromise needs to be found for the layer thickness, whose optimal value depends on the nature of the buffer molecules.

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