Optics and Photonics Journal, 2014, 4, 280-287
Published Online October 2014 in SciRes. http://www.scirp.org/journal/opj
http://dx.doi.org/10.4236/opj.2014.410027

Scientific Research

Investigation on Lanthanum Fluoride as a Novel Cathode Buffer Material Layer for the Enhancement of Stability and Performance of Organic Solar Cell

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Received 5 July 2014; revised 2 August 2014; accepted 27 August 2014

Abstract

This article presents the investigation on very thin Lanthanum Fluoride (LaF_3) layer as a new cathode buffer layer (CBL) for organic solar cell (OSC). OSCs were fabricated with poly(3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM) polymer blend at 1:1 ratio. Electron-beam evaporation at room temperature was used to deposit 3 and 5 nm thick LaF_3 layer. A very smooth surface of LaF_3 with an average roughness of 0.2 nm has been observed by the Atomic Force Microscope (AFM) that is expected to prevent diffusion of cathode metal ion through it and thereby enhance the lifetime and stability of OSC. Huge enhancement of J_{SC} and V_{OC} was also observed for 3 nm-thick LaF_3 CBL. Several excellent features of the LaF_3 layer such as, transporting electron through tunneling, blocking of holes to the cathode, minimizing recombination, protecting the photoactive polymer from ambient oxygen, and reducing degradation/oxidation of any low work function layer at the cathode interface, might have contributed to the performance enhancement of OSC. The experimental findings indicate the promise of LaF_3 to be an excellent CBL material for OSC.

Keywords

Organic Semiconductor, Photoactive Polymer, Organic Solar Cell, Bulk Heterojunction Solar Cells, Cathode Buffer Layer, Lanthanum Fluoride, Spin Coating, E-Beam Evaporation

How to cite this paper: Islam, Md.S., Saklayen, Md.G., Rahman, Md.F., Baerwolff, H. and Ismail, A.B.Md. (2014) Investigation on Lanthanum Fluoride as a Novel Cathode Buffer Material Layer for the Enhancement of Stability and Performance of Organic Solar Cell. *Optics and Photonics Journal*, **4**, 280-287. http://dx.doi.org/10.4236/opj.2014.410027

1. Introduction

Solar cells utilizing organic materials have recently become of great interest due to their potential to utilize high throughput and low-cost solution phase processing [1]-[6]. But, before OSCs can be commercialized practical limitations of OSCs such as low power conversion efficiency (PCE) that results from the low open-circuit voltage (V_{OC}), short-circuit current (J_{SC}) and fill factor (FF) and limited operational lifetime must be overcome. The overall performance of OSCs can be increased by various ways such as controlling the architecture, morphology, processing, and the fundamental electronic processes photoactive layers. Most research has focused on the photoactive layer and control of their morphology to achieve high efficiency of OSCs [7]-[9]. Whereas, performances of OSCs, such as the electron extraction and V_{OC}, are also found to depend largely on the interfacial layers between a photoactive layer and electrodes [10]-[12], and why it is necessary to develop interfacial layers to further improve the efficiency.

Use of appropriate electrodes materials or introducing charge extraction layers can be used to improve V_{OC} and charge extraction of both the electrodes. When a buffer layer is used at the electrodes it produces a non-ohmic contact and the V_{OC} is determined by the difference in work-function between the two electrodes instead of the difference in (HOMO) level of the donor (PCBM) and the lowest unoccupied molecular orbital (LUMO) level of the acceptor (P3HT) for ohmic contact [13]. The stability of the organic solar cell is also a big concern as the cathode-material ion diffuses through the active layer which can react with the polymer and alter its semi-conducting properties [14]. Another degradation phenomenon is the formation of insulating metal-oxide layer at the cathode interface [15]. Therefore, stability can be improved by using efficient diffusion barrier material having less air sensitivity. Improvement of V_{OC} and charge extraction has been done by modifying electrodes or introducing charge extraction layers. Various metal fluorides, TiO_x, and low work function cathodes have been reported to improve the electron injection/extraction contact [16]-[21].

In a quest of finding a new cathode buffer layer (CBL) that will protect the organic layer from the direct deposition of hot Al vapor and prevent damages, act as a diffusion barrier for both Al, exciton and hole and form oriented dipoles at the interface of the organic layer that improves the electron extraction, in this report LaF_3 has been investigated as a new CBL between the polymer bulk-heterojunction and Al-cathode. LaF_3 has been considered because it posses the mentioned features [22] [23]. The main objective of this study is to investigate the effect of incorporation of very thin LaF_3 layer between the photoactive polymer and Al cathode on short-circuit current density (J_{SC}) and open circuit voltage (V_{OC}) of OSC. The effect of annealing on the performance of the OSC has been also investigated. The extremely smooth surface morphology of the e-beam evaporated amorphous LaF_3 layer favours its diffusion barrier characteristics for ambient oxygen and Al ions. Very large ionization potential of LaF_3 favours the blocking characteristics of photogenerated holes. Above all, huge improvement in the J_{SC} and V_{OC} has been observed for a 3 nm thick LaF_3 layer. Experimental results suggest that the possibility of using a thin LaF_3 buffer layer at the Al-cathode could enhance the performance and stability of OSC.

2. Experimental

Readymade blend of P3HT and PCBM at 1:1 ratio and PDOT were bought from Sigma-Aldrich Chemie GmbH Steinheim, Germany. The OSC fabrication began with the deposition of ITO on a properly cleaned glass substrate. Commercially available ITO powder (99.99% pure) was obtained from Inframat Advanced Materials, USA, and was used as the evaporation source material. Electron beam evaporation technique was used to deposit ITO thin films on glass substrate at room temperature using an Edwards E-306, vacuum coating unit. Glass substrates with 140 nm thick ITO film were annealed at 600˚C for 10 min to obtain an optical transparency of >90% and electrical resistivity of 1.25×10^{-5} Ω·m. Hole transport layer (PDOT) was deposited on ITO film by spin coating. On PDOT layer P3HT:PCBM blend was spin coated to obtain a 90 nm thick layer. Then on P3HT:PCBM layer LaF_3 was evaporated. Finally, Aluminium (Al) cathode was evaporated on LaF_3 layer. The device thus formed was annealed in a temperature-controlled furnace in air at 130˚C for 2 min. The resulting structure of the OSC is schematically shown in **Figure 1(b)**.

3. Results & Discussion

The roughness of the cathode buffer layer (CBL) is very important for the performance of the OSC. The light transmission through the layer is decreased and the efficiency of the OSC decreases with the increase in roughness [24] [25]. The roughness of the LaF_3 layer was studied with AFM. **Figure 2** shows the amplitude image of

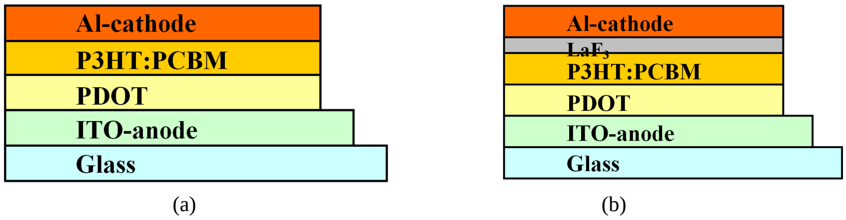


Figure 1. Structure of proposed organic solar cell (a) conventional and (b) proposed.

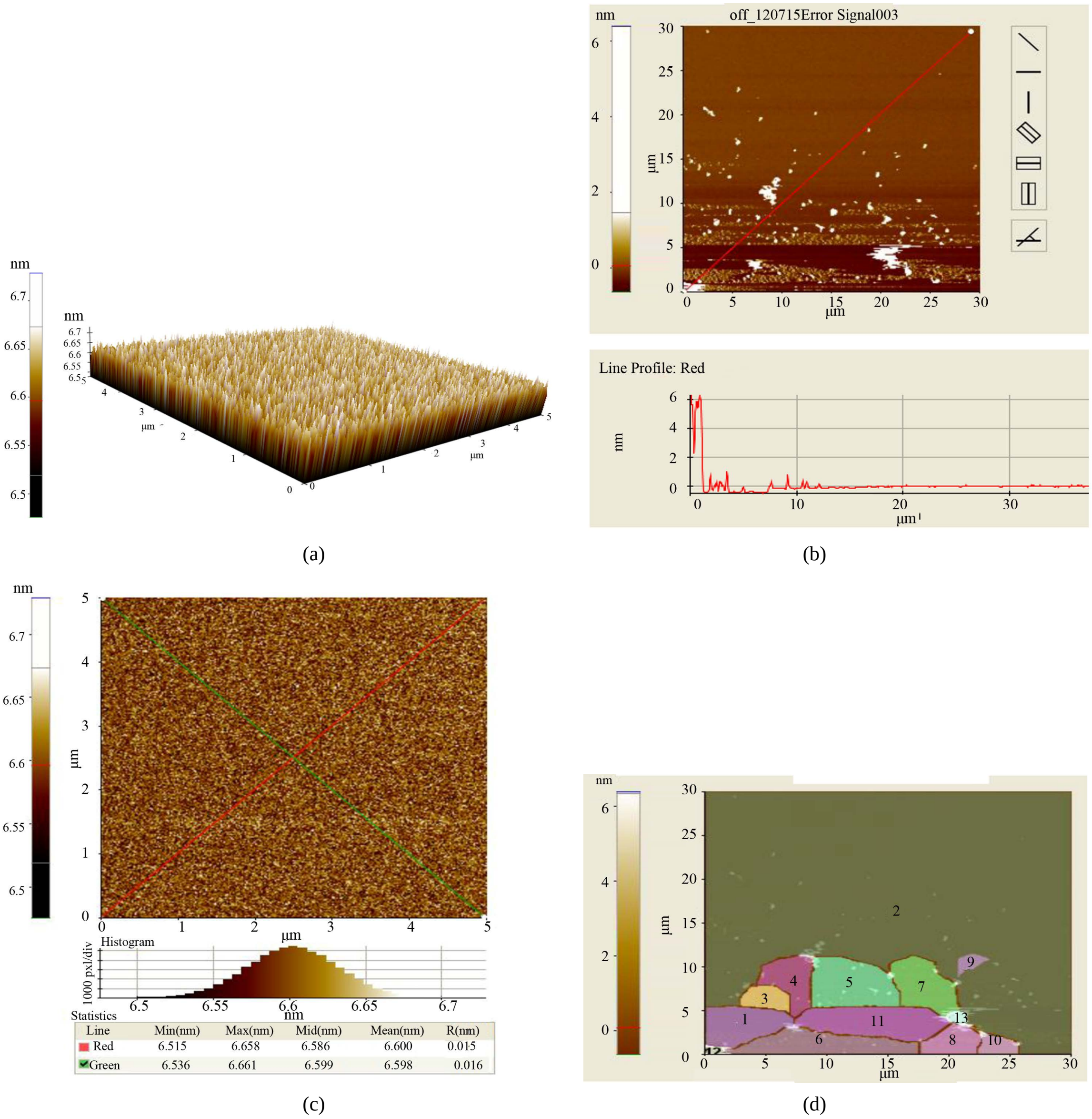


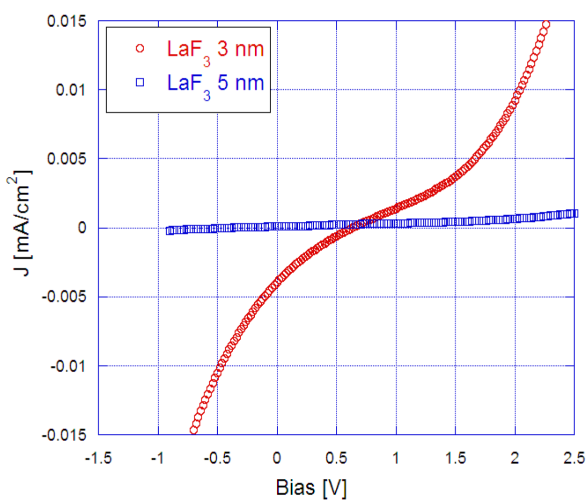
Figure 2. Surface morphology of LaF_3 layer (a) 3D topography and (b) image from error signal showing the thickness measurement and (c) roughness calculation.

the AFM and its corresponding roughness. The LaF_3 layer was selectively deposited on the P3HT:PCBM layer. Then AFM tip was scanned 30 × 30 nm scale at the interface between LaF_3 and P3HT:PCBM layer. As shown in **Figure 2(b)** the peak in the error signal indicated the thickness of the LaF_3 layer. The average roughness was found to be ~0.02 nm. Therefore very smooth surface was obtained by e-beam evaporation.

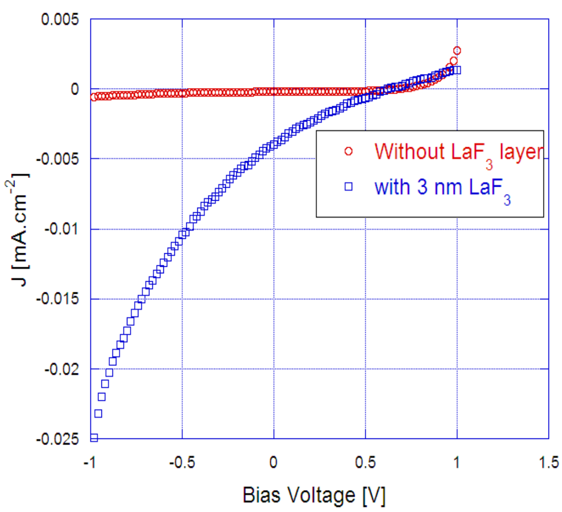
To act as a diffusion barrier layer that prevents diffusion of metal ion, in this case of LaF_3 layer to be the barrier of Al, amorphous films are desired, since grain boundaries between individual crystals would provide a leakage path for the diffusion of ions and lead to device failure [26]. The as deposited LaF_3 films were found to be amorphous and why it is expected that it will prevent Al ion to diffuse into the polymer photoactive layer [26].

The J-V characteristics of the fabricated OSCs (with and without LaF_3 CBL) were studied under forward and reverse bias condition in dark and under 1.5 AM simulated sunlight illumination. The comparison of J-V responses of the two types of OSCs is shown in **Figure 3**. It can be noticed from **Figure 3** that the J_{SC} was small for both the cases. Accordingly, the conversion efficiency, fill-factor of the solar cells was small. This was due to fabrication process used to fabricate the OSC, processing environment, quality of the polymer blend etc. As the mentioned factors were common during the fabrication of the two types of OSCs (with and without LaF_3 layer) the enhancement in performance can be attributed to the incorporation of LaF_3 interlayer. As shown in **Figure 3** huge enhancement in short-circuit current density was observed. The comparative J-V response of the OSCs for three different thicknesses of LaF_3 layer is shown in **Figure 4**. The J_{SC} was proportional to the thickness of the buffer layer. Electron tunneling is impossible with a LaF_3 layer as thick as 5 nm. The reduced J_{SC} can be attributed to the increase in cell resistances induced by too thick layer. Thicker CBL produced no improvement as was reported for other interlayer [27]-[31] for organic light-emitting diodes. For this study it was found that the 3 nm of interlayer LaF_3 thickness showed the performance enhancement of the OSC. Further enhancement in the short-circuit current density was observed when the whole device was annealed at a temperature of 150˚C for 10 minute. **Figure 4** shows the J-V characteristics with and without heat treatment. Similar improvement after annealing at 150˚C for 30 min was observed for PCPDTBT-based solar cell with CdSe-QDs as the Al-cathode buffer layer [32]. It may be due to the improvement of contact between the photoactive material and electrode that arose from the decrease in the concentration of traps at interfaces and smoothing of the film surface. The experimentally obtained open-circuit voltage and short-circuit current density values for various thickness of the LaF_3 layers for the as deposited and after heat treatment are summarized in **Table 1**.

The improvement of V_{OC} can be attributed to the increase of the built-in-potential of the devices with a LaF_3 layer resulting from the upward shift of the vacuum level at the cathode and the enhancement in J_{SC} can be attributed to the efficient electron collection, which can be explained by a tunneling model [33]. **Figure 5** displays the schematic energy-level diagram for conventional OSC and OSC cell with 3 nm LaF_3 CBL. The energy level value has been taken from [34]. The bending of conduction and valence bands becomes much steeper for the OSC with LaF_3 buffer layer than that without LaF_3 layer. Larger built-in-voltage can be expected if the difference in the effective work function between two electrodes is larger. Due to the increased band bending in PCBM excitons generated in the PCBM layer could diffuse to the interface of PCBM/LaF_3 and readily dissociate at the interface under the strong built-in electric field formed from the orbital bending near the junction.



(a)



(b)

Figure 3. Comparative J-V response, (a) with and without LaF_3 and (b) between the two different layers.

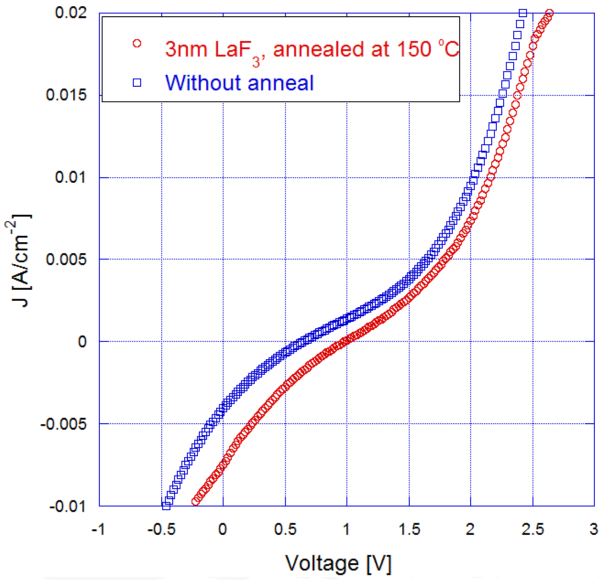


Figure 4. J-V response of the fabricated OSC with LaF_3 buffer layer with and without heat treatment.

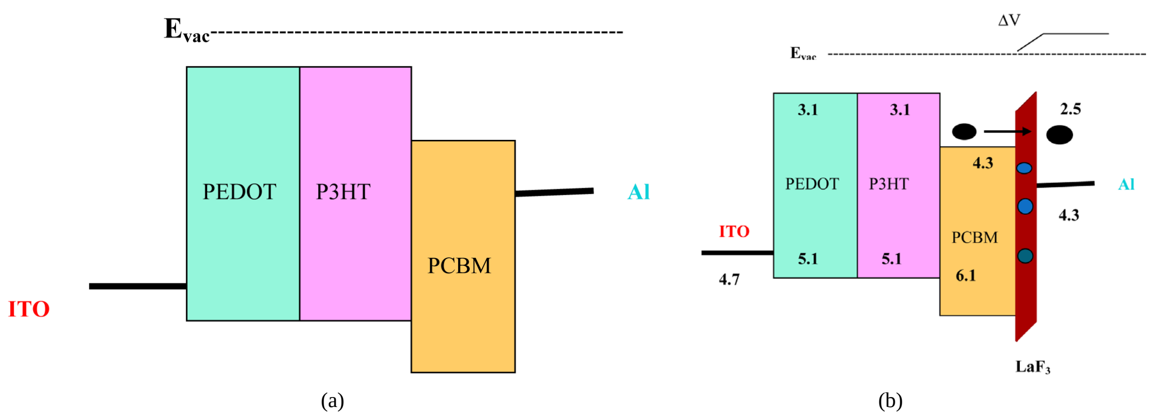


Figure 5. The vacuum level shift and energy levels in OSCs (a) without and (b) with LaF_3 CBL.

Due to increased electrical field the electrons can tunnel through 3 nm LaF_3 layer efficiently [35] [36]. Again, LaF_3 film is an electrical insulator and due to its exceptionally large surface polarization [37] [38] thin LaF_3 layer is expected to decrease the surface potential of the Al cathode and thus the effective work function, resulting in favorable electron extraction. These are all in good consistence with the obtained enhancement in J_{SC} and V_{OC}.

As shown in **Figure 5(b)** the LaF_3 layer can act as hole-blocking layer as the ionization potential of LaF_3 (12.4 eV) is much larger than that of PCBM (6.3 eV). LaF_3 also has a high electron affinity that enhances electron extraction from PCBM and blocks holes as a result probability of radiative recombination is greatly improved. Moreover, recombination at the metal/polymer interface can be avoided as the LaF_3 layer separates the recombination zone from the metal electrode.

4. Conclusion

Thin layer of LaF_3 as a novel cathode buffer layer between the Al cathode and photoactive polymer in an organic solar cell (OSC) in organic solar cell has been investigated in this article. Thinner LaF_3 could induce LUMO/HOMO levels to have a more feasible level alignment for electron transport, and block holes. Substantial increase in the short-circuit current density and open-circuit voltage of the conventional OSC was observed.

Table 1. Summary of the experimental results.

Solar cell parameters	LaF_3 thickness of 3 nm		LaF_3 thickness of 5 nm	
	Without anneal	Anneal at 150˚C for 20 minutes	Without anneal	Anneal at 150˚C for 20 minutes
V_{OC}	0.68 V	1.0 V	0.37 V	0.18 V
J_{SC}	4.3 $\mu A/cm^2$	27 $\mu A/cm^2$	0.0845 $\mu A/cm^2$	3.8 $\mu A/cm^2$

Extremely smooth surface of amorphous LaF_3 as obtained by AFM image favored its diffusion barrier characteristics for ambient oxygen and Al ions that degraded the organic layer and thereby reduced solar cell stability and lifetime. Therefore along with performance enhancement LaF_3 is expected to enhance the stability and lifetime of organic solar cell. All together, very thin LaF_3 can be considered as a very promising material that can be used in organic solar cells as a cathode buffer layer.

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