Improved solar cell performance by adding ultra-thin Alq₃ at the cathode interface

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ABSTRACT

We report a new finding that ultra-thin *Tris*(8-hydroxyquinoline) aluminum (Alq₃) improves an Al cathode interface for photovoltaic (PV) with inorganic amorphous silicon (a-Si) as well as organic bulk heterojunction (BHJ) photoactive layers. Contact resistance characterization is used to investigate the effect of the added Alq₃. The experimental results show that the inserted Alq₃ is observed to reduce the contact resistance at the cathode interface. Supported by our numerical analysis, the enhanced cathode interface by Alq₃ provides better Ohmic contact, thereby increasing V_{oc} . The overall power efficiency is enhanced accordingly benefited by the Alq₃ added cathode regardless of photoactive layers.

KEYWORDS

Solar cells; Cathode interface; Contact resistance; Hybrid photovoltaic

1. INTRODUCTION

Bulk heterojunction (BHJ) organic photovoltaics (OPVs) have shown considerable progress in high efficiency power conversion with simple and low-cost fabrication processes [1-6]. Among BHJ active materials, a blend of poly(3-hexylthiophene) (P3HT) and (6,6)-phenylC61-butyric acid methyl ester (PCBM) has been studied extensively, such as morphology optimization, etc. [1-4]. Yet enhancing contact interfaces between the electrodes and the BHJ active layer still needs to be exploited to mitigate charge recombination and facilitate the collection of electrons and holes [7-10].

Aluminum is often used as a cathode for P3HT:PCBM based BHJs, and a LiF layer added adjacent to the Al layer helps to improve short circuit current density (J_{sc}), open circuit voltage (V_{oc}), and overall power conversion efficiency (PCE) [11]. This significant performance enhancement has been accredited to, among several factors, the improved charge collection due to the better Ohmic contact created by the added LiF layer [11]. However, for such devices it has been widely accepted that there is still opportunity for increasing the efficiency of collecting photogenerated charges at the interface between the photoactive layer and the cathode [12,13].

Among possible electron transport layer (ETL) materials, *tris*(8-hydroxyquinoline) aluminum (Alq_3) is commonly used in organic electroluminescent devices [14-16]. In order to enhance electron injection efficiency, Alq_3 employs a thin LiF at the interface with an Al cathode [15,17]. It has been verified that the interfacial combination of Alq_3 and LiF/Al significantly reduces the barrier height for electrons to injection from the Al cathode to the Alq_3 layer [14,15]. Therefore we anticipate that the Alq_3 /LiF/Al configuration for better cathode contact can be possibly applied to other solid-state devices, e.g. solar cells.

In this work, we report an experimental finding that a cathode configuration with ultra-thin Alq₃, (as compared with the thick Alq₃ used for luminescence devices), can benefit BHJ OPV operation by improving electron extraction efficiency, which accordingly facilitates charge transport and leads to V_{oc} increase. We also experimentally verify that the performance enhancement by the Alq₃ added cathode is not limited to OPV, but applied to inorganic/organic hybrid photovoltaics with amorphous silicon (a-Si). This is simple and effective method for Ohmic contact formation, which was confirmed by contact resistance characterization. In order to further study the effect of the improved Ohmic contact on V_{oc} , we provide a numerical analysis result.

2. EXPERIMENTAL

Solution Casting. Indium-tin oxide (ITO) (sheet resistance of 8-12 Ω) on glass is used as a substrate and anode for the organic solar cells. About 50 nm-thick poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is spin-casted on the ITO layer. For BHJ organic solar cells, a P3HT:PCBM blend is then spin-coated on the PEDOT:PSS. The blend is made by a solution process with a ratio of P3HT:PCBM (10 mg:10 mg) in chlorobenzene (1.0 ml). The final film thickness is ~100 nm. For the P3HT device type, P3HT is also spin-casted to the final thickness of ~40 nm. The P3HT solution is composed of 5 mg P3HT and 0.5 ml chlorobenzene.

Vacuum Deposition. Alq₃ is deposited by thermal evaporation on the organic layers (P3HT:PCBM BHJ, P3HT, and C₆₀) at a deposition rate of 0.1 $\text{\AA s}^{-1}$. For the contact resistance

characterization, a custom-designed shadow mask is used for Al/LiF and Al/LiF/Alq₃ depositions without breaking vacuum. All thermal evaporation processes are operated at a base pressure of 10⁻⁶ mbar. An intrinsic a-Si layer is deposited by a plasma enhanced chemical vapor deposition (PECVD) tool at 240°C (SiH₄ gas with 13.56 MHz RF power).

Electrical Characterization. The performance of devices is characterized by current density-voltage (J-V) measurements. Circular-shaped devices with a 1 mm diameter are tested under illumination by AM1.5 simulated sunlight (100 mWcm⁻²). The intensity of the light is uniformly distributed throughout the cell area by an optical setup. A Keithley 2400 is used for data acquisition in J-V measurement and contact resistance characterization. For contact resistance measurement, the electrodes have different gaps (0.2, 0.4, 0.7, and 1.5 mm) with the same width (8 mm). The deposited contact pads are used for applying a voltage and acquiring a current between the two selected pads by Keithley 2400.

3. RESULTS AND DISCUSSION

An ultra-thin Alq₃ layer (0~3 nm) is inserted between a cathode (Al/LiF) and BHJ blend as shown in Fig. 1a. The current density-voltage (J-V) characteristic of the Alq₃ added BHJ device is compared to a control device without Alq₃ (Fig. 1b). The Alq₃ added device shows the enhanced J_{sc} and V_{oc} with overall enhanced power efficiency. The J_{sc} increase is cannot be attributed to the optical spacer effect since Alq₃ is too thin. The performance of the BHJ devices with the varied Alq₃ thickness layers of 0.3 nm, 0.7 nm, and 3.0 nm is summarized in Table S1 (Supplementary Material). On the average the solar cells with the ultra-thin Alq₃ layer (0.7 nm)

show a PCE of 4.11%, as compared with 3.66% in the control devices, and small standard deviations of 0.11% (Fig. S1) in Supplementary Material. This presents the PCE increase of 12.3% in the Alq₃ inserted OPV.

Fig. 1.

To understand this effect better, we designed and characterized two additional sets of device structures. The first structure, composed of a P3HT photoactive layer instead of BHJ (Fig. 1a), was used to investigate whether the effects are contributed to the cathode interface without the help of PCBM (Fig. 2a). The second structure is a BHJ device using an Al/Alq₃ cathode without a LiF layer, which is compared to a BHJ device with Al cathode (Fig. 2b).

Compared to the P3HT-only device with Al/LiF cathode, the device with Al/LiF/Alq₃ cathode shows a ~0.4 V increase in V_{oc} as depicted in Fig. 2a. Since for PV devices with only donor but no acceptor, V_{oc} is affected by the work function difference between a cathode and an anode, we can presumably infer that the added Alq₃ layer increases the work function difference between the cathode and anode. The cathode work function change (~0.4 eV) is confirmed by

surface potential measurement using conductive atomic force microscopy (cAFM) under dark condition as shown in Fig. S2 (Supplementary Material).

Fig. 2.

For the set of BHJ devices without LiF (Fig. 2b) where the cathodes are in non-Ohmic contacts [18], the devices with Al/Alq₃ cathode attain V_{oc} greater than those with the Al cathode. This increase indicates that the Alq₃ layer creates a better cathode contact as it is well understood that V_{oc} is dependent on electrode contact quality in non-Ohmic cases [18]. Here we acknowledge that, for BHJ OPV with perfect Ohmic contacts, V_{oc} is ideally determined by the offset between the highest occupied molecular orbital (HOMO) level of the donor and the lowest occupied molecular orbital (LUMO) level of the acceptor [3].

The better Ohmic contact at the cathode interface should lead to the reduced contact resistance. For direct experimental verification, we performed contact resistance (R_C) measurement to evaluate the quality of the cathode contact by the Alq₃ insertion. A voltage bias is applied between two cathode contacts interfaced with an organic semiconductor; and the resulting current measured (Fig. 3a). The varied resistances at different gap lengths are linearly related:

$$R = 2R_C + R_{\square} \times \left(\frac{L}{W}\right) \quad (1)$$

Here R is the total resistance between two contact pads, R_C the contact resistance between the metal and the semiconductor, $R_{\square}$ the sheet resistance of the organic semiconductor layer, L the gap length between the contact pads, and W the width of the pads (Fig. 3a).

Fig. 3.

Devices are fabricated with either Al/LiF contacts or Al/LiF/Alq₃ (0.7 nm) contacts. The resistance values between two contact pads are obtained using the linear fit of current-voltage relations as they are linearly correlated in small voltage bias regime. The Al/LiF/Alq₃ cathode device exhibits reduced contact resistance less than 500 kΩ between the cathode and the active layer as compared to the ~2 MΩ for devices with Al/LiF cathode (Fig. 3b). The contact resistance values are obtained from the vertical axis intercepts of the linear fits, as predicted by Eq. (1). We note that the J_{sc} increase shown in Fig. 1b is attributed to the enhanced charge collection by the better contact quality at the Al/LiF/Alq₃ cathode. However, as Alq₃ is a wide bandgap material, there should be an optimal thickness in helping charges transported by

processes such as hopping [19]. For instance, a thick Alq₃ layer (e.g. 3.0 nm in Table S1) showed the lower OPV performance.

Fig. 4.

One question remains unanswered is how the enhanced cathode contact increases V_{oc} as described earlier. To investigate the V_{oc} change by different cathode configurations, we performed simulations to investigate the effect of the work function change on the energy band at the cathode interface. The simulation was performed with solving the continuity equations and Poisson's equation self-consistently [20]: more details can be found in Supplementary Material. Fig. 4a shows the energy band diagram determined from the simulations when the voltage bias across the PV cell is equal to V_{oc} . In the case of Al/LiF/Alq₃ cathode, the reduction of cathode work function provides better Ohmic contact, however there is distinct band bending of the active layer near the cathode. This band bending is caused by the accumulation of high density of electron space charge because the improved Ohmic contact also reduces the electron injection barrier from the cathode [21].

Ideally the built-in potential (V_{bi}) should increase linearly with the increase of the work function difference, but the significant band bending consumes much of this difference. As a result, the actual V_{oc} increase is saturated to a certain level (Fig. 4b). If we define a quasi-flat band voltage (V_{QFB}) [20], a bias voltage that can render the bulk active layer energy band flat, we can observe that the band bending at the cathode affects V_{QFB} in Fig. 4b. Obviously V_{QFB} , correlated with V_{oc} , initially increases with work function difference, but eventually saturates due to the amount of band bending depicted in Fig. 4a. The V_{QFB} increase is also experimentally supported by Mott-Schottky potential change (Fig. S3) in Supplementary Material. Here the device with added Alq_3 at the cathode interface shows larger Mott-Schottky potential than the device with only Al/LiF cathode. Regarding Ohmic contact at the cathode and Schottky junction at the anode, the MS potential corresponds to V_{QFB} [22].

Fig. 5.

This benefit of inserting Alq_3 in a cathode interface is not limited to OPVs. We applied the Alq_3 added cathode configuration to our novel inorganic/organic (a-Si/ C_{60}) hybrid PV structures as shown in Fig. 5a. The a-Si photoactive layer forms Schottky junction with ITO, and

organic C₆₀ is used as electron transport layer as shown in the band diagram of Fig. 5a. Since C₆₀ has a comparable LUMO level to PCBM, we again use a thin layer of Alq₃ inserted to the cathode to interface with the C₆₀ (Fig. 5a). The enhanced cathode interface by Alq₃ dramatically reduces the series resistance of the a-Si hybrid PVs compared with Al/LiF cathode device: from 3.4 k Ω to 1.2 k Ω as shown in Fig. 5b. The series resistance decrease consequently enhances the fill factor (FF) of the hybrid PVs from 35% to 51%: eventually PV power efficiency is much improved. This experimental evidence is well anticipated from the results discussed above regarding OPV device structures. Thus the advantage of applying thin Alq₃ to the cathode interface on PV performance is quite universal and applicable to various photoactive/electron transport material systems. Currently we are working on further enhancing the cathode contact of the a-Si hybrid PVs by employing other organic electron transport materials instead of C₆₀.

In summary, we observed that the overall PV power efficiency factors of BHJ organic solar cells were increased when an ultra-thin Alq₃ was inserted in the interface of Al/LiF cathode to the photoactive layer. The contribution of the cathode interfacial layer to the device behavior was studied in detail by performing various characterizations. The improved Ohmic contact with smaller contact resistance of the Al/LiF/Alq₃ cathode facilitates charge transport and extraction of photogenerated electrons, resulting in the enhancement of V_{oc} as well as J_{sc}. Our numerical analysis supports that better Ohmic contact improves V_{oc} though limited by significant band bending near the cathode. The band bending offsets the benefit of the increased work function difference by the added Alq₃ layer, which is further supported by the Mott-Schottky potential change. More importantly, the effectiveness of the Alq₃ cathode interface can be applied to other PV structures with different material systems as proved in the novel a-Si/organic hybrid PV. Our

experimental results and analysis indicate that careful design of interfacial layer is critical not only for J_{sc} increase but for other PV efficiency factors such as V_{oc} and FF.

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APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary material associated with this article can be found in the online version.

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FIGURE CAPTIONS

Fig. 1. Organic solar cells with the Alq₃ added cathode interface. (a) Device structure with P3HT:PCBM BHJ or P3HT active layers. (b) J-V characteristics of the OPVs with Al/LiF/Alq₃ (0.7 nm) cathode and Al/LiF as a control under photo condition.

Fig. 2. J-V characteristics of organic solar cells with the Alq₃ inserted cathodes under photo condition. (a) P3HT active layers without PCBM electron acceptors with the cathodes of Al/LiF/Alq₃ (0.7 nm) and Al/LiF. (b) BHJ active layers interfaced with Al/Alq₃ (0.7 nm) cathode and Al for a control device.

Fig. 3. Contact resistance characterization of BHJ organic solar cells. (a) Measurement schematics and a shadow mask for electrodes. (b) Measured contact resistance of the Al/LiF/Alq₃ cathode as compared to the Al/LiF, according to the linear fit of the resistance versus gap distance between two electrode pads.

Fig. 4. Numerical analysis of the cathode interface effect on PV performance. (a) Simulated energy band diagrams of BHJ organic solar cells with two different cathodes (Al/LiF/Alq₃ and Al). (b) Numerical analysis results of V_{bi} , V_{QFB} , V_{oc} , and band bending as a function of the work function difference between cathode and anode.

Fig. 5. Inorganic/organic (a-Si/C₆₀) hybrid PV structures with the Alq₃ added cathode interface. (a) Device structure with a-Si photoactive layer and C₆₀ electron transport material (inset: band diagram of the hybrid PV). (b) J-V characteristics of the hybrid PV structures with Al/LiF/Alq₃ (1 nm) cathode and Al/LiF as a control under photo condition.