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Electron beam versus thermal deposition of aluminum top electrode for organic solar cells

Abduleziz Ablat*, Lionel Hirsch, Mamatimin Abbas

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Abstract

The current-voltage characteristics and photovoltaic parameters of polymer solar cells with Al cathode separately deposited by thermal and electron beam methods were compared. The power conversion efficiency of as prepared electron beam deposited device is ten times lower than that of thermal evaporated one. However, after post-annealing, device performance parameters of electron beam deposited device sharply increased and reached almost the same values as thermal evaporated device. Through the analysis of J-V characteristics in the dark, the formation of deep traps at the interface induced by electron beam, as reported in earlier studies, was excluded.

Keywords: organic solar cells, Al cathode, electron beam deposition, thermal evaporation

1. Introduction

Organic semiconductors have seen significant development in recent years and been used to make ultrathin, large area, flexible and cheap organic electronic devices. As a result of intensive chemical design and synthesis efforts, the performances of bulk heterojunction organic solar cells (OSC) have been rapidly improved in recent years. Nowadays, the power conversion efficiency (PCE) of organic solar cells has reached above 15% with newly emerged organic semiconductors [1–3]. The current record has been set using a ternary blend i.e. PM6:BTP-eC9:PC71BM solar cell devices[4]. In conventional direct solar cell structure, Al cathode is by far the most commonly used metal for extracting electrons, either alone or together with other interfacial layers[5–7]. The Al deposition methods such as electron beam (e-beam), sputtering and thermal evaporation can have strong effect on the performances of the devices [8,9]. Thermal deposition of Al contact is known to be rather cumbersome. Spreading of molten Al, easy breakage of crucible due to alloy formation and the difficulty in controlling the deposition rate are the main issues. All these issues can be avoided with e-beam deposition technique. However, the energetic

e-beam radiation may cause possible damage to the organic layer and thus rarely been used in the OSC fabrication process. Researchers did apply e-beam to deposit Al cathode electrode for P3HT:PCBM OSCs and compared it with thermal evaporation, achieving even higher open circuit voltage (V_{oc}) after post annealing treatment. The improved V_{oc} was attributed to the formation of metal-polymer complex interlayer [9] or interface dipoles between the organic photoactive layer and metal electrode[10]. Especially, the formation of interface dipoles that resulted from deep interfacial traps were proposed based on minimum current (“current zero”) in dark J-V curves.

In this letter, we report that e-beam deposited Al electrode does not induce deep traps on organic semiconductor layer as reported earlier. Indeed, the initial performance of OSCs are quite low comparing to thermally evaporated Al cathode devices. However, the performance parameters can be largely improved following an annealing treatment, reaching similar values.

2. Experiment

We fabricated direct structure solar cell devices, where indium thin oxide (ITO) and Al served as anode and cathode electrodes, respectively. In a typical procedure, ITO substrates were treated by UV/ozone for 10 minutes after usual cleaning process (sequentially with de-ionized water, acetone, ethanol, and isopropanol in an ultrasonic bath for about 30 minutes). Then, filtered poly (3,4-ethylenedioxythiophene):poly (4-styrenesulfonic acid) (PEDOT:PSS) suspension was spin coated on top of the ITO under ambient condition as hole transporting layer. PEDOT:PSS film was annealed at 110 °C for 1 hour. The solution of poly (3-hexylthiophene-2,5-diyl) (P3HT) and [6, 6]-phenyl C₆₁ butyric acid methyl ester (PCBM), dissolved in chlorobenzene at a concentration of 20 mg/ml with a mass ratio of 1:0,7 was spin-coated (2000 rpm for 60 s) directly on top of PEDOT:PSS in nitrogen glove box. Finally, Al cathode was deposited on P3HT:PCBM photoactive layer through shadow mask by thermal evaporation or e-beam deposition in vacuum under base pressure of 4×10^{-6} mbar (the schematic diagram of the device and chemical structures of photoactive layer are shown in Fig.1). The light and dark current-voltage (J-V) characteristics of OSC devices were measured using Keithley 2400 source

meter. The light current was measured under AM 1.5G condition simulated by a HMI lamp, calibrated to 100 mW/cm^2 using a radiometer (International Light, IL1400BL).

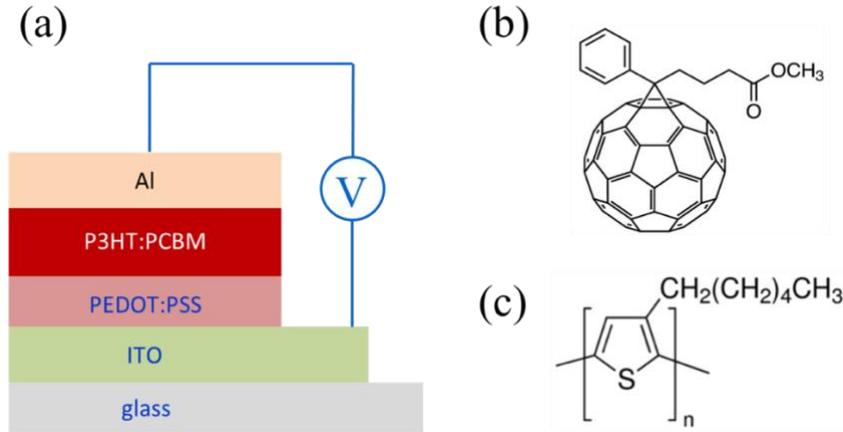


Fig. 1. (a) Schematic diagram of the device structure of organic solar cell. Chemical structures: (b) PCBM and (c) P3HT.

3. Results and discussion

Fig.2 shows under light J-V characteristics of P3HT:PCBM solar cells with Al cathodes deposited by e-beam and thermal evaporation. As fabricated devices are presented together with the devices annealed at $160 \text{ }^\circ\text{C}$ for 10 minutes. We have observed a very large difference in device performance for as fabricated devices. J_{sc} , FF and V_{oc} are $1,79 \text{ mA/cm}^2$, 26,5%, 227 mV for the e-beam deposited device, instead $5,75 \text{ mA/cm}^2$, 40%, 471 mV for the thermal evaporated device. However, after thermal annealing at $160 \text{ }^\circ\text{C}$ for 10 minutes, both devices show similar J_{sc} , FF and V_{oc} ($8,13 \text{ mA/cm}^2$, 60,3%, 609 mV for the e-beam deposited device, and 8 mA/cm^2 , 60,7%, 608 mV for the thermal evaporated device). These results indicate that even though the initial organic/metal interaction is very different for the devices when fabricated by different electrode deposition methods, after post annealing, both device reach a similar interaction at organic/metal interface. Indeed, for as fabricated devices, the series resistance is much higher in e-beam deposited device ($277 \text{ } \Omega$) than that of the thermal evaporated one ($64 \text{ } \Omega$). Series resistance affects all other device performance parameters. To understand such a difference, we measured the substrate temperature during the evaporation process. We observed that the substrate temperature raised to $46 \text{ }^\circ\text{C}$ when thermal evaporation was used, whereas the substrate temperature during the e-beam deposition remained at room

temperature. Clearly, slightly heated substrate played a critical role in improving the metal/active layer interaction. After post annealing the devices at 160 °C, both series resistances decreased respectively to 19 Ω and 15 Ω, explaining the almost similar devices performances. Comparison of device performance parameters are given in Table 1.

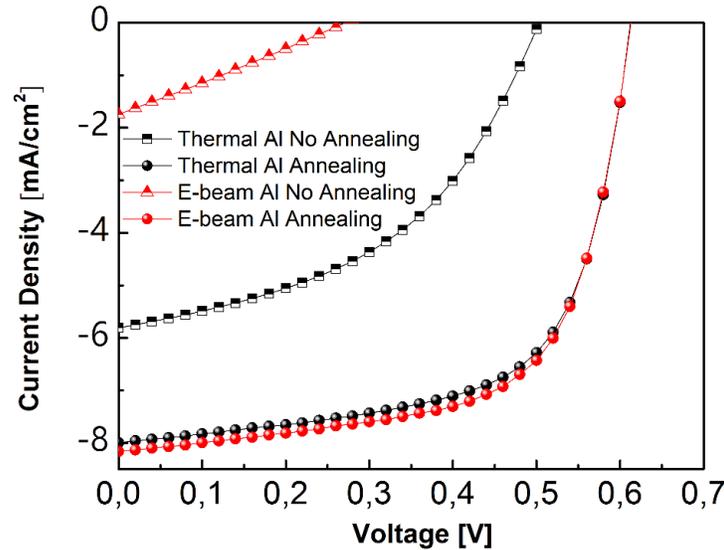


Fig.2 J-V characteristics under light of typical P3HT:PCBM solar cells as fabricated and after annealing at 160 °C with Al cathode deposited by e-beam and thermal evaporation.

Table 1 Average photovoltaic performance of solar cells as fabricated and after annealing at 160 °C with Al cathode deposited by e-beam and thermal evaporation, measured under AM 1.5G simulated by a HMI lamp (100 mW/cm²). Eight devices were tested for each condition.

Sample	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)	R_s (Ω)	R_{SH} (kΩ)
as prepared (e-beam)	1,79 ± 0,48	0,227 ± 0,057	26,5 ± 0,5	0,10 ± 0,07	276,8±23,3	0,32±0,21
as prepared (thermal)	5,75 ± 0,77	0,471 ± 0,012	39,9 ± 5,2	1,11 ± 0,22	64,2±9,5	1,56±0,70
160 °C (e-beam)	8,13 ± 0,12	0,609 ± 0,008	60,3 ± 4,3	2,99 ± 0,24	18,7±5,2	2,19±1,08
160 °C (thermal)	8,00 ± 0,22	0,608 ± 0,004	60,7 ± 3,1	2,95 ± 0,12	14,9±0,6	3,65±1,92

In order to investigate temperature effect on device performance, we illustrated detailed device parameters of the solar cells annealed at various temperatures in Fig.3. After annealing at 130 °C, both devices showed almost the same device parameters and the PCE

difference largely decreased, which also corresponds to the realignment of series resistance of these two devices. Further increasing of the temperature induces the optimization of nano-morphology of the active layer, and the maximum PCEs were obtained for both devices after annealing at 160 °C.

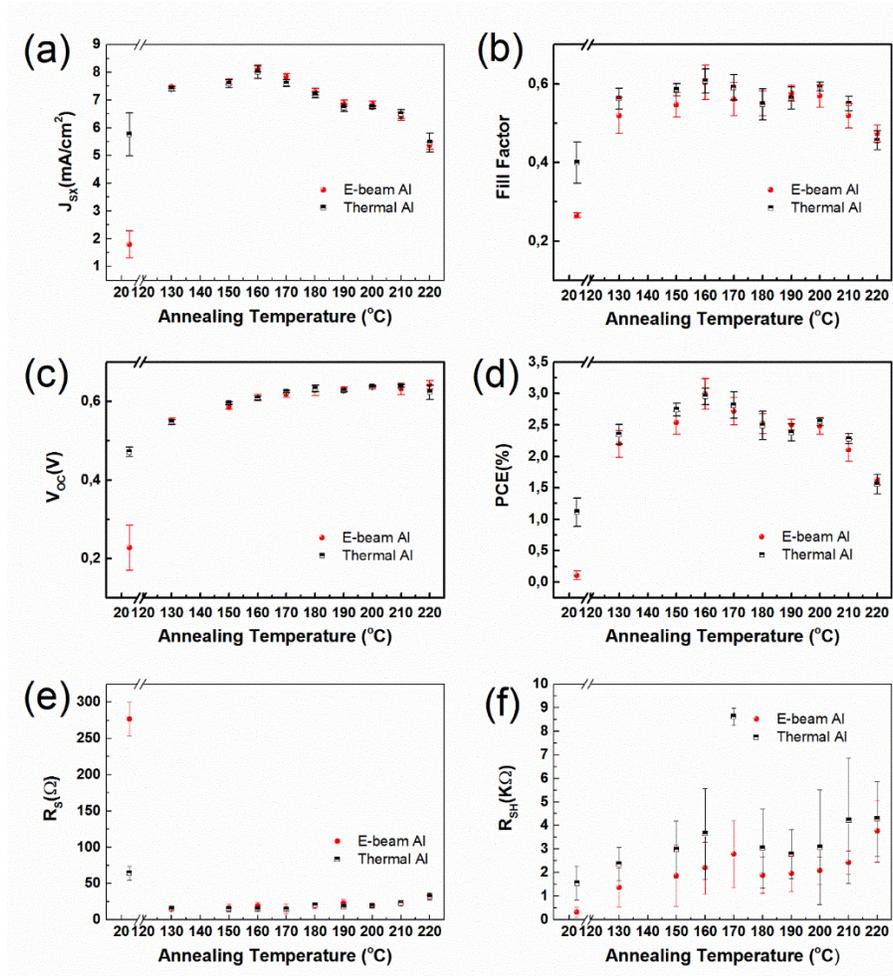


Fig.3 The average (a) J_{sc} , (b) Fill factor, (c) V_{oc} , and (d) PCE, (e) Series resistance (R_s) and (f) Shunt resistance (R_{sh}) of solar cells with e-beam deposited Al cathode and thermal evaporated Al cathode at varying annealing temperature for 10 minute.

We investigated the effect of the e-beam on the active layer. Fig.4 shows dark J-V characteristics of both devices as fabricated and after annealing at 160 °C for 10 minutes. The inset images are the enlarged dark J-V characteristics from -0,5 V to 0,5 V. As shown in Fig.4, both devices yield minimum current (“current zero”) when the voltage is zero. In addition, there is no shift of current zero for both devices after post annealing (as clearly seen from the inset in Fig.4). This finding is in contrast to the work of Zhang et al.[10] who

observed a large shift of the current minimum in e-beam deposited devices, and attributed it to the deep traps created in the active layer[11]. Our study proves that the active layer is free from such deep traps caused by e-beam.

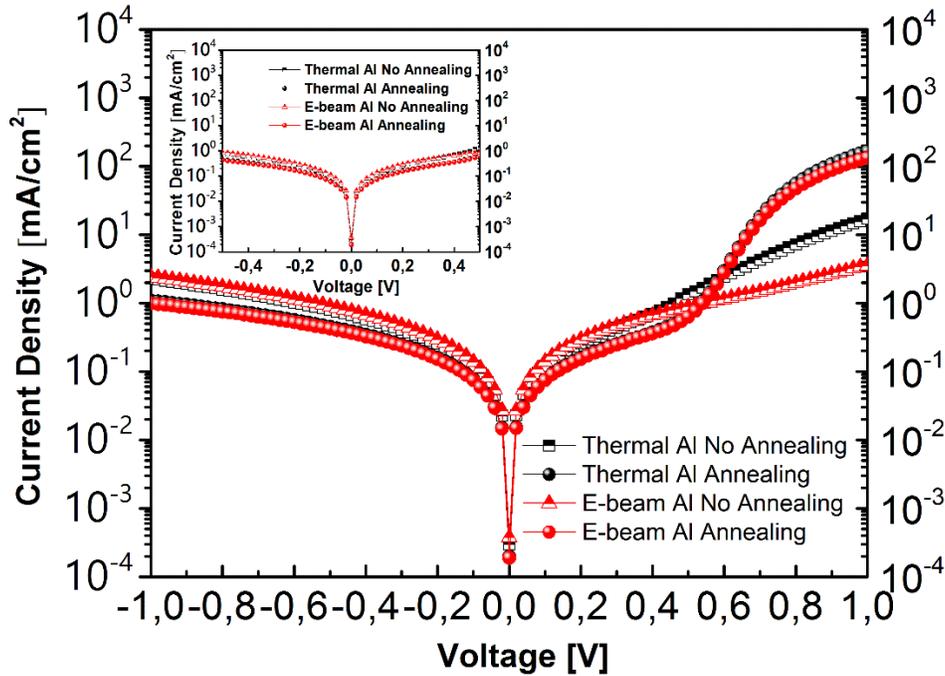


Fig. 4 Dark J-V characteristics of typical P3HT:PCBM solar cells with e-beam deposited Al cathode and thermal evaporated Al cathode as fabricated and after annealing at 160 °C for 10 minutes. The inset images are the enlarged dark J-V characteristics from -0,5 V to 0,5 V.

In summary, detailed investigation of P3HT:PCBM solar cells parameters and J-V characteristics confirmed the nonexistence of deep interfacial traps in organic layer when e-beam was used for Al deposition. Although as prepared e-beam deposited device showed much lower performance than thermal evaporated device, similar performances could be achieved after post annealing at 130 °C. These obvious increases of OSC parameters in e-beam deposited Al cathode device after post annealing are attributed to the better interface interaction between the active layer and electrode following thermal treatment, which is largely hampered in as prepared device. This is mainly due to relatively low substrate temperature nature of e-beam deposited device comparing to the thermal evaporated

device. Our study proves that e-beam is a safe and efficient method to deposit cathode metals, especially Al, for organic solar cells.

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