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The working mechanism of organic photovoltaic cell by using copper phthalocyanine as exciton blocking layer

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ABSTRACT

We demonstrate the working mechanism of organic photovoltaic (OPV) cell with copper phthalocyanine (CuPc) as exciton blocking layer (EBL). The new EBL material CuPc, commonly has been used as electron donor in the organic solar cells due to its electron-donating and hole-transporting properties. But here we proves that the α-polymorph CuPc layer can transfer electrons to Al cathode through the half-filled b_{1g} level, this mechanism is different from that of general EBL material with larger band gap and electron-transporting property, which is based on damage states induced by the heat of evaporating Al.

1. Introduction

Organic photovoltaic (PV) cells are being promising photodiodes because of their mechanical flexibility, ease of fabrication and potential for low-cost solar energy conversion [1–4]. In these devices, no matter planar- or bulk-heterojunction (HJ) under illumination, excitons are generated in the photoactive layers and diffused to donor (D)/acceptor (A) interface, and then some excitons would be dissociated into free electrons and holes at the D/A interface by level offset between D and A molecules, subsequently these charge are collected by two electrodes to contribute the photocurrent [5]. At the same time, other excitons far from the D/A-HJ may be recombined, which substantially lower the power-conversion efficiency (PCE) [6,7]. Many technologies have been employed to improve the OPV PCE, such as using mixed D/A structure or materials with long exciton diffusion length [8]. As is expected, encouraging progress has been made with PCE of 8.3% [9] for small molecule organic solar cell with an active area exceeding 1 cm^2.

In the case of CuPc/fullerene (C_{60}) bilayer OPV cell, the EBL have been inserted between C_{60} and cathode for the improvement of PCE. Forrest group [10] has introduced bathocuproine (BCP) as the EBL in CuPc/C_{60} bilayer OPV cell, its PCE has increased to 3.6% under AM1.5 illumination. The ideal EBL serves many functions, the main role is to prevent damage that resulted from heat metal cathode deposition and thereby eliminating exciton quenching at the accepter/cathode (A/C) interface [10]. Certainly, ideal EBL material should transport charge to ensure low cell series resistance. Simultaneously, the EBL may act as a spacer to place the region of highest optical intensity at the D/A-HJ [11], but thin BCP can not play this role.

The most typically used EBL materials have wide energy gap and hence transparent semiconductors, such as bathophenanthroline (Bphen) and BCP, they can transport electrons via the damage states induced by heat metal

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deposition. Still on the one hand, thick layer would be unsuitable for these EBL materials due to their large energy gap and the depth of the damage states. Doping or using the combination with low-resistance organic materials could overcome this shortage partly [12,13]. On the other hand, the better stability was obtained by choosing CuPc as EBL rather than BCP [14]. For these reason it may be desired to replace BCP with another material in the future. In order to find such a substitute, the working mechanisms of CuPc EBL in OPV cell need to be understood in more details.

In this work, BCP, Bphen, 4,4′,4″-tris (*N*-3-methylphenyl-*N*-phenylamine) triphenylamine (m-MTDATA), β-naphthylphenylbiphenyl diamine (NPB) and CuPc were respectively used as EBL in the OPV cells with structure of ITO/CuPc/C_{60}/EBL/Al. And we found that the thickness of the EBL affects the PV performance obviously. While the thickness of EBL is less than 10 nm, the electrons were transferred through the damage states induced by heat Al deposition [10], but this mechanism could not be adopted for explanation the photocurrent curvilinear trend when the thickness of CuPc EBL larger than 10 nm. It is worth mentioning that the electronic structure of α-polymorph CuPc, the b_{1g} level lies at where higher than the highest occupied molecular orbital (HOMO) level about 0.8 eV [15]. So we think the photo-generated electrons could be transferred through the b_{1g} level of the α-polymorph CuPc layer to cathode during the thickness of CuPc EBL at 10–30 nm.

2. Experimental details

Commercially available ITO coated glass substrates with a sheet resistance of 10 Ω/□ were used. The organic materials for fabrication were procured commercially and were used without further sublimation. Before the organic films were deposited, the substrates were initially scrubbed in detergent solution. They were then immersed sequentially in a heated ultrasonic bath of acetone, deionized water and acetone for 30 minutes, respectively. Finally, the substrates were treated by UV lamp for 15 minutes.

Table 1
The parameters of the materials.

Buffer layer	LUMO (eV)	HOMO (eV)	Electron mobility (cm^2/V s)	Hole mobility (cm^2/V s)
BCP	3.5 [16]	7.0 [16]	5.0×10^{-6} [17]	–
Bphen	2.9 [18]	6.4 [18]	5.0×10^{-4} [18]	–
CuPc	3.5 [16]	5.2 [16]	9.0×10^{-4} [19]	7.0×10^{-4} [20]
C_{60}	4.5 [21]	6.2 [21]	5.1×10^{-2} [20]	–

The prepared substrates were loaded into ultra-high multi-source thermal evaporation vacuum chamber with base pressure of 2×10^{-4} Pa. Deposition rate of 1 Å/s was maintained for organic materials, 8–12 Å/s for Al. Thickness of each layer was measured using calibrated quartz crystal thickness monitor. A 20 nm thick CuPc and a 40 nm thick C_{60} were used as the donor and the acceptor, respectively. The thicknesses of BCP, Bphen m-MTDATA, NPB and CuPc EBLs were varied. A shadow mask was used for the deposition of the cathode. The active area of the devices was 2×5 mm^2. The solar cells with different exciton blocking layers were respectively fabricated and the PV performances were compared. Current–voltage (*I*–*V*) characteristics were measured with a programmable source meter (Keithley-2400) in the dark and under AM1.5 solar illuminations at intensity of 100 mW/cm^2 of solar simulator. The light intensity was measured with a calibrated Si-solar cell. The crystalline morphology of the films was determined using a Rigaku D/MAX-2500V diffractometer in the Bragg–Brentano configuration with a CuK_α source. All measurements were carried out at room temperature and under ambient conditions without any protective coatings.

3. Results and discussion

Fig. 1 shows the *J*–*V* curves of PV devices with structures of ITO/CuPc(20 nm)/C_{60}(40 nm)/EBL(10 nm)/Al, here EBL is BCP, Bphen and CuPc, respectively. And the parameters of the materials are shown in the Table 1. Note that the

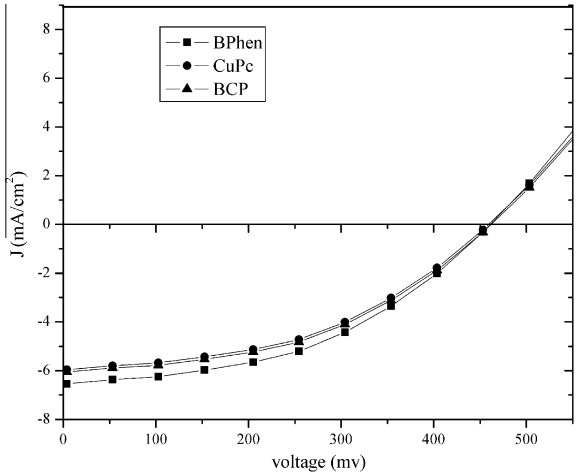

Fig. 1. *J*–*V* curves of ITO/CuPc/C_{60}/EBL/Al devices with BCP, Bphen, CuPc under illumination with an intensity of 100 mW/cm^2, respectively.

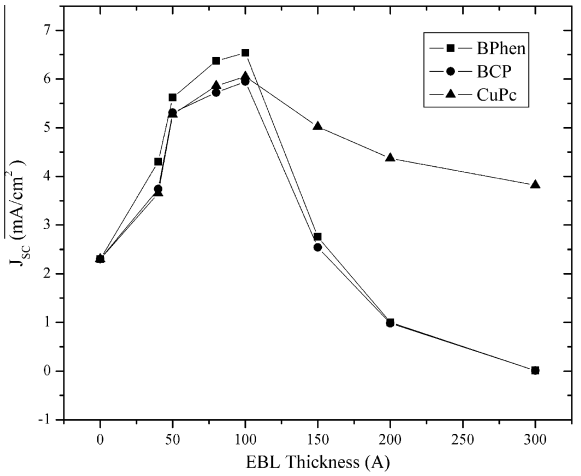

Fig. 2. J_{sc} as a function of BCP (▲), Bphen (■), CuPc (●) thickness under illumination with an intensity of 100 mW/cm^2.