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Effects of idling time between depositions of organic layers and metal electrode in organic photovoltaic device

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ABSTRACT

Deposition of metal cathode in organic photovoltaic (OPV) devices is known to cause serious metal atom penetration into the active layers and as a remedy, exciton blocking layer (EBL) is implemented. It is found that the metal penetration through EBL can be controlled by optimizing the idling time between the depositions of EBL and cathode layers. Both electrical and optical data show that the resistance of BPhen layer (EBL) to metal (Mg:Ag) penetration increase with increasing idling time. Also, significant variation in power conversion efficiency (PCE) is observed in subphthalocyanine chloride (SubPc)/fullerene (C_{60}) based organic photovoltaic (OPV) cells by simply adding idling time as an additional control parameter. Device with optimized BPhen thickness and idling time resulted in a PCE of 2.8% whereas that of no idling time consideration has PCE limited at 2.3%. These observations are attributed to slow processes of self-organization in BPhen after their depositions.

1. Introduction

Organic photovoltaic (OPV) device is considered as a next generation solar cell with merits of low cost, lightweight etc [1–4]. Performance enhancement has been achieved by both employing better light harvesting materials and smart device structures [2,5–11]. For example, the introduction of an exciton-blocking layer (EBL) between the acceptor and cathode considerably enhances performance of OPV devices by keeping the excitons from the metal electrode and thus reduces quenching [12,13]. It has been shown that the thickness of EBL has critical influences on the device performance [14]. Upon deposition of the cathode, defect levels will be formed in the EBL and they are considered to provide a high conductance pathway for extracting electrons to the external circuit. Therefore, the EBL should be thin enough such that the defect levels can be formed in most of its thickness. On the other hand, it should also be thick enough such that the defect levels will not spread considerably into the active layer [15–17]. In most OPV devices, bathocuproine (BCP) or bathophenanthroline (BPhen) of about 7 nm is used as the EBL.

In this work, we study the effects of idling time between the depositions of the EBL and the cathode. We found that efficiency of SubPc/C_{60}/BPhen device can vary significantly by fine tuning the idling time between depositions of the EBL and the cathode. We further show that the penetration depth of the metal atom decreases with increasing idling time. These results suggest that after deposition of the EBL, its molecules will be self-reorganized in vacuum. In our case, it takes about 20 min for a 7 nm thick BPhen film to reach a stable compact structure to keep metal atom penetration from the active layers. After roughly estimating the extent of metal atom diffusion for different idling times for a constant thickness of EBL, we have optimized the EBL thickness for each idling time separately. Simultaneous optimizations of both the idling time and the EBL thickness resulted in an overall PCE of 2.8%. On the other hand, the PCE was limited to 2.3% by only optimizing the EBL thickness while using the minimal idling time allowed by the deposition system. This 23% PCE enhancement suggests that the idling time is a long ignored processing parameter for optimizing device performance. This work also shows that in typical device processing conditions, there will be structure changes in solid films of small organic molecules immediately after their depositions.

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2. Experimental

Patterned ITO-coated glass substrates with a sheet resistance of 30 Ω/square were routinely cleaned with Decon 90, rinsed in deionized water, dried in an oven, and finally treated in an ultraviolet–ozone (UV–ozone) chamber for 15 min [18]. A series of devices were fabricated by thermal evaporation with a structure of: ITO/SubPc (12.5 nm)/C_{60} (42 nm)/BPhen (7 nm, kept in 10^{-6} Torr for T = 10, 15, 20, 25 and 30 min)/Mg:Ag (100 nm). The base pressure and the deposition pressure was always maintained at ~1×10^{-6} Torr and <3×10^{-6} Torr, respectively. 'T' is the idling time between deposition of BPhen and the cathode. 10 min is the minimal idling time in our system needed for heating up the metal evaporation sources. The BPhen thickness of 7 nm is chosen based on reported value in the literature [19]. All small molecule materials including SubPc, C_{60}, BPhen (from Luminescence Technology Corp) were used as received. All the organic layers were grown at a deposition rate of 1–2 Å/s; whereas the Mg:Ag cathode was grown at ~10 Å/s with a volume ratio of 9:1. The active device area is 0.1 cm^2. All these devices were encapsulated in a glove box immediately after fabrication [20]. An Oriel 150 W solar simulator using a programmable Keithley model 237 power source was used for characterizing the current density–voltage (J–V) properties of the devices in both dark and under AM 1.5G simulated solar illumination.

3. Results and discussions

Fig. 1 summarizes the device performance when ITO/SubPc/C_{60}/BPhen samples is idled for T = 10, 15, 20, 25 and 30 min before Mg:Ag deposition for a BPhen thickness of 7 nm. While the devices of T = 10 and 15 min show similar PCE of ~1.8%, the device of T = 20 min shows almost 38% improvement in PCE to ~2.5% (Fig. 1a). In particular, the J_{sc} increases from 3.9 to 4.5 mA/cm^2 (Fig. 1b), whereas the V_{oc} improves from 0.92 to 1.08 V (Fig. 1c). When T further increases to 25 and 30 min, the PV enhancement becomes saturated with overall PCE vary by less than 10% compared to T = 20 min device. These results point out that immediate deposition of cathode after EBL deposition can result in poor photo conversion efficiency.

To further investigate the variation in performance, the dark current density and the external quantum efficiency (EQE) of these devices are studied. Fig. 2a shows the J–V characteristics of devices under dark. It is noteworthy that device with T = 20 and 25 min exhibit low leakage current (−0.03 mA/cm^2 at −1.5 V) comparing to T = 10 and 15 min devices (>−0.30 mA/cm^2 at −1.5 V). This observation might be due to reduced defect sites in the C_{60} layer [21]. Besides, the low leakage current is also due to the increase in shunt resistance. The slope of J–V curve at 0 mA/cm^2 is much smaller for devices with T = 20 and 25 min, which reflects higher shunt resistance in these devices. The dark J–V characteristics suggest that there are less defect states in the device with T = 20 and 25 min. The observed leakage current reduction leads to V_{oc} improvement [22]. By analyzing the dark current carefully, we found 2 different types of device properties in this study. (1) Ohmic diode behavior dominated: in Fig. 2a, devices with T = 10 and 15 show ohmic behavior with very high conductivity. This is due to the metal doping of C_{60} during metal deposition. The metal atoms penetrate into C_{60} and break down the Schottky diode behavior of SubPc/C_{60} junction. (2) Schottky diode behavior dominated: devices with T > 20 show Schottky diode behavior. Compact BPhen layer has enough resistance to block the metal penetration to the C_{60} layer.

In order to understand the difference in photo responses in all these devices, their EQE spectra are measured and shown in Fig. 2b. When the time interval T increases, the photo response of SubPc (at ~580 nm) shows negligible changes. However, the photo response of C_{60} (340–550 nm) is significantly improved.

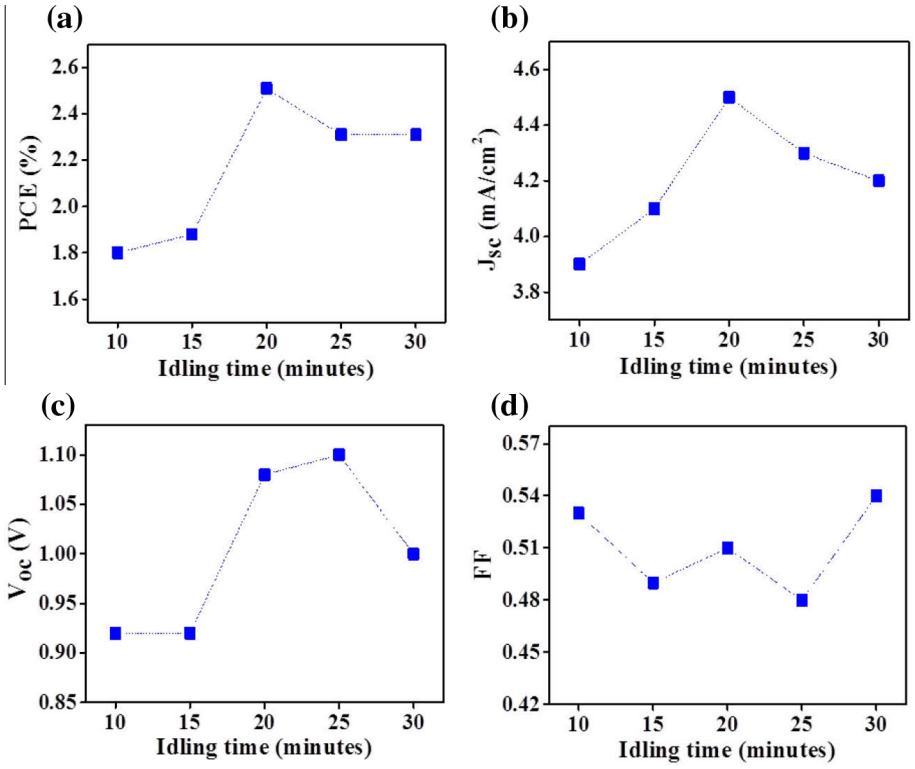

Fig. 1. Photovoltaic response of devices with the structure of ITO/SubPc (12.5 nm)/C_{60} (42 nm)/BPhen (7 nm)/Mg:Ag showing the (a) power conversion efficiency; (b) short circuit current density; (c) open circuit voltage; and (d) fill factor as a function of the increasing idling time T between BPhen and Mg:Ag deposition.