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A transparent conducting oxide as an efficient middle electrode for flexible organic tandem solar cells

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ABSTRACT

We demonstrate an efficient middle electrode of indium zinc oxides (IZOs) for flexible organic tandem solar cells. A bulk hetero-junction polymer solar cell and a bi-layer hetero-junction organic solar cell are used as the bottom and top cell, respectively. Insertion of a thin interfacial layer of Rb_2CO_3 or Cs_2CO_3 between the polymer and IZO and UV–ozone treatment of the IZO surface results in Ohmic contact with the top and bottom cells, respectively. The tandem devices showed that the open circuit voltage (V_{oc}) was almost the same as the sum of the V_{oc} of the individual cells with a fill factor of 0.57. The tandem devices fabricated on flexible PES substrate showed comparable results.

1. Introduction

Organic photovoltaic (OPV) cells have attracted attention as a promising renewable energy source because of the potential for low cost production of energy, simple fabrication process and high flexibility [1]. The power conversion efficiency (PCE) of organic solar cells has increased steadily for the last few years and reached values over 6% for polymer single cells [2–5] and over 5% for organic single solar cells [6]. The PCEs, however, are still too low for commercial application. Stability and manufacture also present equally large challenge [7]. Inorganic silicon-based solar cells, which are already in the market, show power conversion efficiencies of more than 14%, and may last on the order of 25 years. Tandem solar cells, which are simply two stacked photovoltaic cells with different absorption spectra in series through a middle electrode, are suggested as an approach to increase the efficiency [8].

Fabrication of tandem solar cells requires multilayer coating. Multilayer solution processing requires orthogonal solvents or cross linking to prevent dissolution of the bottom layer during the over-coating without any sacrifice of charge transporting properties and has always been a largely unsolved problem not only in OPVs but also in OLEDs [9]. This difficulty of multilayer solution processing has been solved in this paper by using vacuum deposition for subsequent layers.

The middle electrode in tandem solar cells also needs to be designed properly not to degrade the efficiency of the devices. First, it should be transparent in the visible to near-infrared region, where organic active materials absorb light to generate photocurrent. Ultrathin metals [10–17] and transparent conducting oxides (TCOs) [18–20] have been used to satisfy this condition. In addition, the middle layer should form Ohmic contact with both the top and bottom cells. For this reason, multiple layers of thin metal and oxide layers [15,19–23] have been introduced.

Hiramoto et al. [8] used a thin gold interstitial layer between unit solar cells, and the photo-voltage was increased by about two times. Since then, thin layers of metal like Ag [10–11,13], Au [8,17], LiF/Al/Au [15], Sm/Au/PEDOT:PSS [21], LiF/Al/WO_3[22] and Al/MoO_3[23] have been used as the middle layer. Metals have high electrical conductivity but also a reflective surface, which gives poor transmittance. Therefore, it is hard to insert more than a few nano-meters of metals between cells without sacrificing optical transmission, which would reduce the short circuit current.

TCOs are good candidates as the middle electrode because of their excellent optical transparency combined with good electrical conductivity. TiO_x has been used as the middle electrode in polymer tandem solar cells to get a high efficiency of 6.5%, where the valence band and the conduction band edge are well matched with the HOMO level of the electron donating material and the LUMO level of the electron accepting material in the top and bottom cells, respectively [18]. However, the energy levels of TCOs and the energy levels of organic materials do not match very

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well, which means that they do not form Ohmic contacts to either collect electrons from one cell or holes from the other cell. Kenji et al. have sputtered ITO between the top and bottom cell, but ITO alone does not have the proper energy levels to extract both electrons from bottom cell and holes from top cell, which is shown by the reduced open circuit voltage of the tandem device [19]. ZnO has also been used as the middle layer without much success to form Ohmic contact with both the top and bottom cells [20]. Therefore, it is very valuable to develop methods to form Ohmic contacts between TCOs and both electron donating (hole transporting) or electron accepting (electron transporting) materials in order to use TCOs as a middle electrode. Moreover, in order to fabricate the device on plastic substrates, the electrode must be flexible under repeated bending. In this report, we employed surface modifications of indium zinc oxide (IZO) to form Ohmic contacts. We used IZO because it can be deposited at room temperature with adequate optical transmittance combined with good electrical conductivity and flexibility [24]. We inserted a very thin layer of LiF, Rb_2CO_3[25] or Cs_2CO_3[26] between IZO and one solar cell of the tandem structure to extract electrons from the cell. The other side of the IZO surface was treated with UV–O_3 for efficient hole extraction from the other cell. Using the surface modified intermediate electrode, we were able to fabricate organic tandem solar cells with the fill factor (FF) of 0.57 and the open circuit voltage (V_{oc}) of 0.96 V, which is almost the same as the sum of the V_{oc} of the individual cells. The performances were almost the same on glass or plastic substrate. In order to solve the difficulty of depositing sequential layers by using a solution-based process, a solution processed bulk hetero-junction polymer solar cell and a vacuum processed bi-layer hetero-junction organic solar cell are used as the bottom and top cell, respectively.

2. Experimental

The ITO-coated glass substrate was successively cleaned with acetone and isopropyl alcohol. The substrate was exposed to UV–O_3 for 10 min before use; 40 nm-thick highly conducting PEDOT:PSS (Baytron P) was spin coated on the substrates and was dried at 140 °C for 15 min in air. The P3HT and PCBM were purchased from Rieke metals and Nano/C, respectively, and were dissolved in dichlorobenzene to make 1:1 wt. ratio solution (40 mg mL^{-1} total). The solution was stirred at 50 °C for 14 h and spin coated onto PEDOT:PSS coated substrates. P3HT:PCBM films have a thickness of 190 nm for single bottom cells and 120 nm for tandem cells. Interfacial layers including LiF, Rb_2CO_3 or Cs_2CO_3 were thermally evaporated on the active layer with a thickness of 0.5–1 nm, followed by the deposition of an IZO film as the middle electrode. IZO was deposited by the facing-target sputtering technique, which was designed to minimize plasma damage on the bottom cell materials. We have used IZO instead of ITO as the intermediate electrode, for it gives high conductivity and transmittance when deposited at room temperature. Moreover, it is flexible without the formation of cracks under repeated bending [24]. The bottom cells were thermally annealed on a hotplate at 130 °C for 10 min in a glove box. The IZO surface was exposed to UV–O_3 for 10 min followed by successive deposition of copper phthalocyanine (CuPc), C_{60}, 2,9-dimethyl-4,7-dipheyl-1,10-phenanthroline (BCP) and Al to complete the fabrication of the tandem devices. The photocurrent was measured under illumination from an AM1.5 solar simulator (300 W Oriel 91160A). Light intensity was carefully calibrated by using a standard silicon solar cell (NREL). Current density–voltage characteristics were measured with a Keithley 237 source measurement unit.

3. Results and discussion

Fig. 1a–c shows the device structure, the energy levels, the absorption spectra and transmittance of the films of each material used in the tandem cells. The charge separation layer in the bottom cell is the bulk heterojunction formed by the P3HT:PCBM blend. The top cell has a layered heterostructure of CuPc and C_{60}. The energy diagram indicates that IZO alone does not form Ohmic contact with both the top and bottom cells. The top and bottom cells have complementary absorptions; yet they have some overlap at wavelengths around 600 nm. IZO shows high transparency over a broad range of wavelengths. The transmittance of 300 nm-thick IZO at around a wavelength of 600 nm, which is the absorption maximum of CuPc, reaches almost 90%, including the absorption of glass. As we have sputtered only 50 nm of IZO

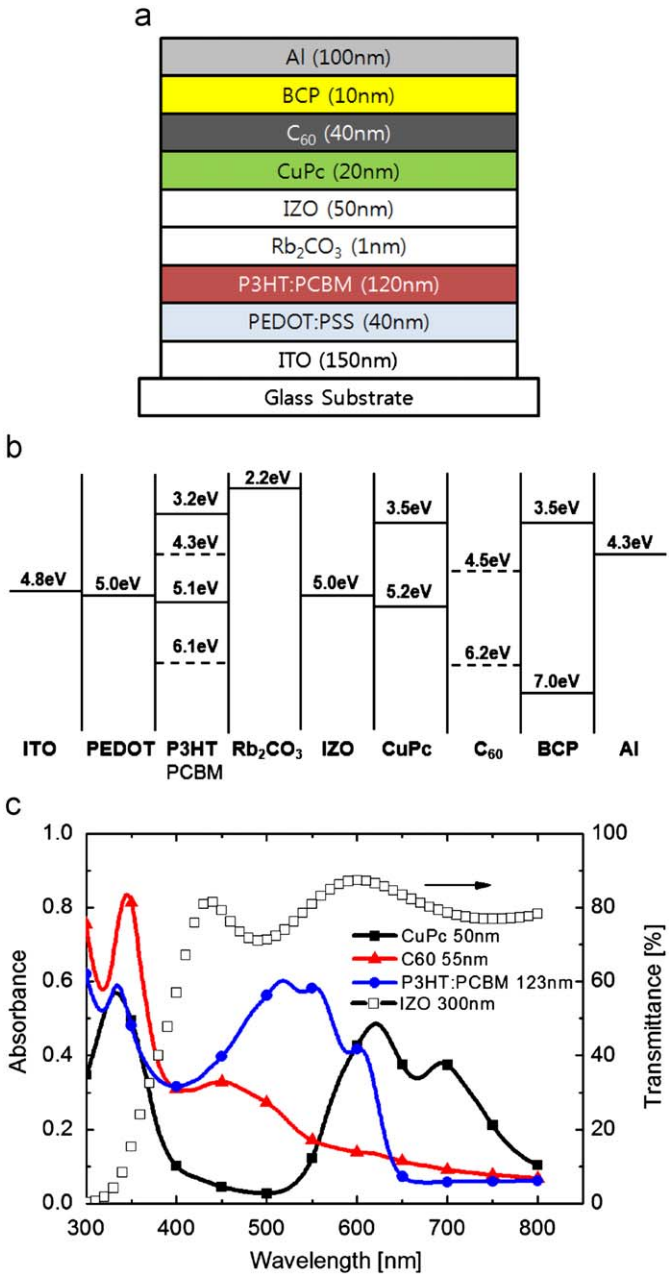

Fig. 1. (a) Device structure, (b) energy diagram of the hybrid tandem solar cell and (c) UV–visible absorption spectra of P3HT:PCBM, CuPc and C_{60}w, and transmittance of IZO.