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Effect of 3,4,9,10-perylenetetracarboxylic bisbenzimidazole (PTCBI) as well as bathocuproine (BCP) and Ag interlayer thickness on the performance of organic tandem solar cells

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ABSTRACT

Firstly, multi-fold subphthalocyanine (SubPc) homo-tandem cells were fabricated. When complementary absorbing SubPc and chloroaluminum phthalocyanine (ClAlPc) were used to prepare tandem cells, both short circuit current (J_{SC}) and fill factor (FF) are significantly improved relative to the SubPc double tandem cell. 3,4,9,10-perylenetetracarboxylic bisbenzimidazole (PTCBI) as electron transporting layer (ETL) in the charge recombination zone (CRZ) achieves a much higher FF than bathocuproine (BCP) thus higher power conversion efficiency (η_{PCE}) in both the normal and reverse tandem cells, ascribed to the matched energy levels, very smooth film surface, and ohmic contact with Ag interlayer. The effect of Ag interlayer thickness was also investigated. Ultrathin Ag layer with isolated clusters is helpful for obtaining higher photocurrent in both PTCBI and BCP based CRZs, originating from a flatter interface, less optical loss, and a plasmonic effect induced absorption enhancement of C_{60} in bottom subcell. By optical modeling for current matching, the performance of normal tandem cell is improved, exhibiting a high open circuit voltage of 1.80 V and an overall η_{PCE} of 3.49%.

1. Introduction

Single junction organic photovoltaics (OPVs) has made great progress in the last few years, and high efficiency beyond 10% based on novel polymer and solution-processed small-molecule materials or special nano-structures has been achieved [1,2]. Tremendous research effort has been made by regarding material designs and physical mechanisms governing the device operation. However, subjected to the absorption property of single donor or acceptor in single cells which usually covers only a fraction of the solar spectrum, single OPVs show limited short circuit current (J_{SC}). Complementary absorbing materials based tandem OPVs could eliminate the obstacles mentioned above, and reduce thermal relaxation losses. The polymer or small molecule based tandem cells have achieved high power conversion efficiency (η_{PCE}) over 10% [3,4]. A polymer homo-tandem cell and a triple-junction polymer tandem cell show the best η_{PCE} of 11.3% and 11.5%, respectively [5,6].

Strategies for improving the performance of tandem cells includes reasonable combination of donor/acceptor materials [7,8], modification of transparent conducting electrode or intermediate layer [9], exploitation of novel buffer layers [10], thickness optimization of sub-cells (SCs) [11], application of plasmonic effect [12], and fabrication of microcavity composed of two or more spacer layers and top capping layer et al. [13]. Optical spacer was used to shift the optical field distribution inside the active layers for the inverted OPVs [14]. Besides the rational material design and efficient interface engineering, the fabrication process of tandem cells has also made advances, such as, fully printed as well as air-processed tandem cells [15,16]. In addition to the conventional series-connected tandem cells, recently emerged semi-transparent parallel-connected tandem cells also received much attention, and the quantitative analysis of the color

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properties was carried out by drift-diffusion modeling from the transmission spectra [17].

Among these strategies, optimization of charge recombination zone (CRZ) under the identical active layers is a simple and effective method. In small-molecule tandem cells, 3,4,9,10-perylenetetracarboxylic bisbenzimidazole (PTCBI) and bathocuproine (BCP) are the most popular electron transporting layers (ETLs) in CRZ. The *trans*- and *cis*- PTCBI were previously used as non-fullerene acceptors in single OPVs [18,19], and a slightly higher efficiency for the *trans* isomer was attributed to a higher exciton diffusion length (L_D) [20]. The rubbing-induced horizontal orientation of PTCBI and its effect on L_D and OPV performance was investigated as well [21]. After the highly efficient fullerene appears, PTCBI has been gradually employed as cathode buffer layer in single or tandem cells [22,23]. In spite of the wide application of PTCBI on single OPVs, there is limited reports on the study of the effect of PTCBI as well as BCP and Ag interlayer in the CRZ for a given tandem cell architecture.

In this work, the effect of PTCBI, BCP, and Ag interlayer thickness on the performance of chloroaluminum phthalocyanine (ClAlPc) and subphthalocyanine (SubPc) based tandem cells was investigated. These particular donor materials are known for their high absorption coefficients and open circuit voltage (V_{OC}) [24,25]. Direct electrical evidence of strong influence of PTCBI, BCP, and Ag interlayer thickness on short circuit current (J_{SC}) and fill factor (FF) is obtained. A relatively higher performance is achieved with current matching by tuning active layer thickness.

2. Experimental

All devices were produced on indium tin oxide (ITO) glasses (Thin Film Devices Inc.) with a sheet resistance of 15 $\Omega\,sq^{-1}$. The substrates were cleaned consecutively using detergent, deionized water, acetone, and isopropanol in an ultrasonic bath and exposed to UV-ozone for 15 min prior to use. The organic materials, ClAlPc (sigma, 85%), SubPc (Lumtec, 99%), PTCBI (Aldrich, 98%), and BCP (Wako Co., 98%) were purified by vacuum gradient sublimation prior to use. While MoO_3 (Aldrich, 99.99%) and C_{60} (MRT, 99.8%) were used as received. The film thickness was controlled by independent quartz crystal microbalance. The Ag cathode was deposited through a shadow mask giving an active area of 0.024 cm^2.

Current density vs. voltage (*J-V*) characteristics in the dark and under the illumination of AM1.5 G (100 mW/cm^2) were measured from a Newport Oriel solar simulator using a Keithley 2400 sourcemeter in air without encapsulation. External quantum efficiency (EQE) measurement was performed using mechanically chopped monochromatic light from a Xe arc lamp in conjunction with a monochromator (Bunko Keiki M25-T), which is same for both the single and tandem cells. The absorption spectra were recorded with a spectrophotometer (LAMBDA 950-PKA, PerkinElmer). The highest occupied molecular orbital (HOMO) energy levels were measured by ultra-violet photoelectron spectroscopy (AC-2, Riken Keiki Co.), and the lowest unoccupied molecular orbital (LUMO) energies were determined by the low-energy optical absorption edge positions relative to the HOMO level. Atomic force microscopy (AFM) images were obtained using a scanning probe microscope (JEOL JSPM-5400, Japan) by tapping mode.

Simulation of EQE spectra for SCs in tandem structures were performed using the transfer matrix formalism with refractive index and extinction coefficient of all the layers, which were measured using a fast spectroscopic ellipsometer (M-2000U, JA Woollam Co.) [26–29]. The simulations assume illumination with AM 1.5 G light. J_{SC} in the SCs was calculated using the transfer matrix method under the following assumptions: that all excitons reaching the donor/acceptor (D/A) interface in the SCs are completely dissociated, and that the charges are collected at the electrodes or without losses at the bottom SC/top SC interface [26–28].

3. Results and discussion

3.1. SubPc based single cell and multi-fold tandem cell

Fig. 1(a) shows the molecular structures of ClAlPc, SubPc, C_{60}, PTCBI, and BCP. The layer stack of the tandem cells is schematically shown in Fig. 1(b). Efficient recombination between SCs has been shown using thin metal layers, highly doped organic layers, or metal-oxides [30–32]. In our work, the SCs are connected by a CRZ consisting of 5-nm PTCBI or 5-nm BCP as ETL, thin Ag, and 2-nm MoO_3 as hole extraction layer (HEL). Fig. 1(c) depicts the energy-level diagram of tandem cells, and PTCBI shows matched energy level with C_{60}.

Fig. 2(a) depicts AM 1.5G spectrum and the absorption coefficient of donors and C_{60}. ClAlPc indicates near infrared absorption and a much higher absorption coefficient than SubPc at the peak wavelength. SubPc shows complementary absorption with ClAlPc, suggesting a good potential of fabricating tandem cells with the donor combination of SubPc and ClAlPc. Fig. 2(b) illustrates the absorption coefficient of PTCBI and BCP. PTCBI shows about half of the peak absorption coefficient of SubPc, while BCP is almost transparent in the visible-light region. The inset shows the AFM images of 20-nm pristine PTCBI and BCP films on ITO substrates. BCP film demonstrates a much higher root mean square (RMS) roughness than PTCBI film.

The effect of SubPc thickness on the performance of single planar heterojunction (PHJ) of SubPc/C_{60} is investigated with varied thickness from 7 to 22 nm. 9-nm-thick SubPc achieves the highest η_{PCE} of 2.88%, which is likely to be related to the reported L_D of 9.4-nm for SubPc [33]. Too thin or too thick SubPc induces lower J_{SC} or S-shaped *J-V* curve, ascribed to the low hole mobility of about 3×10^{-5} $cm^2/V\,s$ [34]. However, the reported performance of ClAlPc/C_{60} single PHJs shows no significant dependence on the ClAlPc thickness [35]. To improve the V_{OC} and η_{PCE} of single junction, SubPc based double and fourfold tandem cells were fabricated under the fixed CRZ as follows:

Single cell: ITO (100 nm)/MoO_3 (2 nm)/SubPc (9 nm)/C_{60} (32.5 nm)/BCP (10 nm)/Ag (80 nm).

Double cell: ITO (100 nm)/MoO_3 (2 nm)/SubPc (9 nm)/C_{60} (20 nm)/PTCBI (5 nm)/Ag (0.2 nm)/MoO_3 (2 nm)/SubPc (13 nm)/C_{60} (25 nm)/BCP (10 nm)/Ag (80 nm).

Fourfold cell: ITO (100 nm)/MoO_3 (2 nm)/SubPc (7 nm)/C_{60} (15 nm)/PTCBI (5 nm)/Ag (0.2 nm)/MoO_3 (2 nm)/SubPc (9 nm)/C_{60} (15 nm)/PTCBI (5 nm)/Ag (0.2 nm)/MoO_3 (2 nm)/SubPc (11 nm)/C_{60} (15 nm)/PTCBI (5 nm)/Ag (0.2 nm)/MoO_3 (2 nm)/SubPc (13 nm)/C_{60} (20 nm)/BCP (10 nm)/Ag (80 nm).

Fig. 3(a) demonstrates the *J-V* characteristics of single, double, fourfold tandem cells. V_{OC} noticeably increases from 1.03 V for the single cell to 3.79 V for the fourfold tandem cell. SubPc based tandem cells show much higher V_{OC} relative to the reported ClAlPc tandem cells with same folds because of larger interface energy gap of SubPc/C_{60} than ClAlPc/C_{60} [25,35]. V_{OC} values are nearly the summation of that of the single cell, demonstrating a negligible voltage loss because of the effective CRZ for an ohmic connection between the neighboring SCs [35]. However, η_{PCE} decreases with more stacking of SubPc SCs. An S-shaped *J-V* curve appears for the double tandem cell and the induced FF is 0.487, stemming from the imbalanced hole and electron transport at the CRZ [36]. The inset indicates the EQE spectra for the three devices, and the EQE value at 580 nm decreases from 38% for the single cell to 13% for the fourfold tandem cell.