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Solution processed cathode and interconnecting layer of silver nanowires in an efficient inverted tandem organic solar cells

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ABSTRACT

Due to the potential of achieving high conductivity and high transparency, low-cost, large-area and flexibility for versatile applications as organic solar cells, silver nanowires (AgNWs) have attracted great attention as a good alternative to conventional ITO. However, design and production of conducting transparent film and interconnecting layers plays a very important role to achieve a high device performance. We discuss the benefit of the AgNWs inserted in the organic tandem solar cell devices as transparent electrode (TE) and as interconnecting layer (ICL) between the two subcells having actives layers with complementary absorption and made of poly(3-hexylthiophene):indene-C_{60} bisadduct and polythieno [3,4-b]thiophene/benzodithiophene: phenyl-C_{71}-butyric acid methyl ester. ZnO nanoparticles have been used as interfacial layer in the ICL and lead to a decrease of the AgNWs roughness. The tandem cells on AgNWs show a good efficiency (PCE=9.23%), a short circuit current density of 11.23 mA/cm^2 close to the lower short circuit current of the two solar subcells, and an open circuit voltage (Voc=1.47 V) matching the sum of the two subcells Voc. This suggests that the ICL provides a good carrier injection through the interfacial layer and an efficient recombination of the current coming from each subcells. Moreover, optical modeling is done in order to calculate the optimized active layers thicknesses and short term stability in open air evaluated.

1. Introduction

Solar energy is a very promising alternative source of energy as it is clean and sustainable. The Bulk heterojunction (BHJ) solar cells offer considerable hope for meeting some of these requirements. [1] Their potential for low-cost and fast roll-to-roll production as well as their light weight and fabrication on flexible substrates could give them major advantages over traditional inorganic solar cells. Recently, 11.3% power conversion efficiency (PCE) was obtained by Heeger and coworker by using the homo-tandem (PTB7-th) bulk heterojunction polymer solar cells (PSCs). [2] however, the best efficiency was obtained by Yussoff and coworker [3] with PCE=11.83% on tandem with triple-junction. The performance of PSCs is dependent on many factors such as active layer materials, [3] device structures and interfaces between different layers. [4] Among them, the transparent electrodes should provide high optical transparency in the visible/NIR (near infrared) range, high conductivity, mechanical flexibility under significant tension/compressive forces, proper adhesion to the polyethylene terephthalate (PET) and glass substrate, environmental stability and chemical compatibility with the other PSC layers and work function alignment with the other device constituents.

Traditional transparent conducting electrodes Indium Tin Oxide (ITO) are widely used in liquid crystalline displays, as well as in number of electronics devices such as polymer solar cells, organic light emitting diodes, thin-film inorganic solar cells, and touch screems. Rapid growth of these products has caused an increased demand of ITO despite the strained supply of indium. Furthermore, the future of the display technology is likely to require flexible electrodes for applications mentioned above. [3–5] ITO is completely unsuited for such applications due to its brittleness. Indeed, ITO was shown some fragility by crocking when used in some applications as touch screen displays, and consequently it is likely to do so in next-generation bendable devices (displays and/or flexible solar cells). [6–8] Moreover, this material needs specific techniques of deposition (evaporation) difficult to integrate in roll-to-roll production lines. Then, it is clear that an ITO substitute is needed, preferably a material whose conductivity is invariant under flexing and dispensed with eco-friendly solvents. [9] Among the conductors films employed in PSC electrodes, many different metallic oxides were explored for electrodes applications as, zinc indium tin oxide (ZITO) [10,11] SnO_2 doped-zinc oxide ($ZnSnO_3$), [12] Indium doped ZnSnO (InZnSnO) [13] and amorphous silicon indium tin oxide (a-InSiO). [14] However, few metallic oxides have

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achieved a low sheet resistance (< 20 Ω/sq) as a-ZITO, but they cannot be deposited with roll-to-roll or printing process, or have a limited optical transmission. Otherwise, high-conductivity poly (3,4-ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT: PSS), [15–17] carbon nanotubes (CNTs), [18] and graphene, [19] have been the most investigated. However, to date, these materials have yielded modest performance mainly due to their relatively low conductivity. Furthermore, corrosive PEDOT:PSS can compromise device stability [21] while CNT and graphene electrodes are challenged by manufacturing costs. [18] Recently, Krebs and coworker [20] proposed a new electrode more enviromentaly friendly for organic photovoltaics (OPV) as cupper and aluminum. However, the electrodes based on AgNWs have demonstrated a low sheet resistance, high conductivity and good flexibility. [21–26] This approach can be a good alternative to replace the ITO substrates. Many creative strategies have been introduced in order to use the AgNWs films. For example, ZnO/AgNWs/ZnO transparent conducting films developed recently by Vedraine and coworkers [26a,27]. AgNWs mesh covered with polyvinyl alcohol, [28] drop-casted AgNWs laminated on PEDOT:PSS films, [29] and AgNWs mesh buffered with a titania (TiOx) or PEDOT:PSS film, [30] have been also recently reported. All these strategies showed good optoelectronic characteristics and have been used as transparent electrodes for high-efficiency organic optoelectronic devices (single and tandem cells).

In the other hand, tandem devices architectures have been demonstrated as a useful approach towards fabrication of high performance cells, where two sub-cells are stacked in series or in parallel. However, organic tandem solar cells based on complementary absorption materials have exhibited [31] PCEs more 10%. Compared to single junctions, tandem cells allow reduction of transmission losses by absorbing low energy photons in a small bandgap cell and reduction of thermalization losses by absorbing high energy photons in a wide bandgap cell. [31,32] The maximum efficiency is, however, only slightly higher than the record efficiency of a single-junction organic cell, suggesting that there is a great room for improvement in the design of multi-junction organic solar cells.

Six years ago, the lack of efficient low-bandgap polymers [33–36] showing high V_{OC} and external quantum efficiency (EQE) at long wavelengths has led to a limitation of the efficiency of polymer tandem solar cells of about 7%. Yang Yang and coworkers in 2008 proposed to use a low bandgap polymer PBDTT-DPP which exhibited an improved quantum efficiency (EQE~50%) at long wavelength. They successfully achieved an inverted tandem PSC [31] with a certified PCE of 8.6%. [37,38] Recent progress on the tandem polymer PV paved a solid ground for achieving higher efficiencies, bringing this concept to a real OPV technology breakthrough. Recently, Heeger and coworker [2] have been achieved an efficiency of 11.3% by using the low bad-gap polymer named poly[4,8-bis-(5,2-ethylhexyl) thiophen[3,2-b:20,30-d]pyran)-alt-4,7-(5,6-difluoro-2,1,3 benzothiadiazole)] (PTB7-Th). The bandgap of this polymer is 1.30 eV. High hole mobility and deep HOMO level have been achieved. [2] Another challenge in order to realize the tandem organic cells with a good performance (high current density and open circuit voltages (V_{OC})) by replacing the famous transparent conducting electrode and a new inter-connecting layer. [2,26,39].

Herein, we have successfully employed AgNWs processed solution in tandem PSCs as transparent conducting films and interconnecting layer sandwiched between ZnO nanoparticles and modified PEDOT:PSS for more efficient charge-transfer by increasing the conductivity of the film, which allow to improve the photovoltaics performances. However, AgNWs films suffer from porosity, weak adhesion, high roughness and is rather sensible to process at temperature higher than 200 °C [46]. Using a soft thermal annealing (140 °C) and a ZnO thin top layer on AgNWs, we improved the performances of the solar cells. All layers were deposited by spincoating except the cathode layer (Ag) by evaporation which could be deposited by solution process. As a results, the PCE of tandem PSCs on AgNWs of 9.23% is achieved with higher current density (11.23 mA/cm^2) more than that on ITO (11.01 mA/cm^2). This work shows the manufacturing and modeling of the efficient inverted tandem organic solar cells with AgNWs based anode and interconnecting layers which plays a very important role to achieve a high device performance, we finished this work by stability studies in air of this devices.

2. Experimental details

2.1. Materials

The acceptor fullerene derivatives, i.e., phenyl-C_{61}-butyric acid methyl ester.

(**PCBM**), indene-C_{60} bisadduct (**ICBA**), phenyl-C_{71}-butyric acid methyl ester (**$PC_{71}BM$**), the donor polymers and small molecule, i.e., poly(3-hexylthiophene) (**P3HT**), polythieno[3,4- b]thiophene/benzodithiophene (**PTB7**) at high molecular weight (100KDa),), and all of the solvents, including solvent additives, were purchased from Sigma-Aldrich. The Ag NW ink was purchased from Cambrios.

2.2. Single-junction devices fabrication

(references devices) ITO substrates, were cleaned by water, acetone, isopropanol, and finally cleaning with UV/ozone. As-received dispersion containing AgNWs (Cambrios Clear Ohm Ink) was spincoated on glass substrates at 2000 rpm and annealed at 100 °C, 10 min. ZnO nanoparticles (Genies 'ink') were spin-coated at 1600 rpm on AgNWs and at 2400 rpm on ITO substrates, annealed at 140 °C, 60 s and treated by UV/ozone, 1 min. The first active layer (P3HT:ICBA) were dissolved at (50%, 50%) CB and o-DCB (20 mg mL^{-1}) and was deposited by solvent annealing process (spincoated at 800 rpm, 30 s). The thicknesses of the P3HT:ICBA layer were checked using a surface mechanical profilometer (150 nm). PTB7-$PC_{71}BM$ (1:1.5) were dissolved in 60% o-DCB, 40% chlorobenzene, at a concentration of 10 mg mL^{-1} and spin-coated at 1400 rpm (110 nm) or 1500 rpm (100 nm). A MoO_3 layer deposited by spincoating (10–15 nm) and silver layer (80 nm) was deposited using a thermal evaporator operating at ~5×10 $^{-6}$ Torr.

2.3. Tandem solar cells fabrication

ZnO nanoparticles (genies 'ink') were spincoated on the ITO (20 nm) and AgNWs substrates and annealed at 140 °C for 60 s. The active layer of the front subcell (P3HT:ICBA) was then spin-coated on the ZnO surface. Then, thermal annealing treatment at 130 °C for 5 min was applied. Next, PEDOT:PSS (40 nm) was spin-coated on the top active layer (P3HT:ICBA) and annealed at 110 °C, 5 min. Then, a 50 nm thick AgNWs was spin coated at 4000 rpm and annealed at 100 °C, 60 s. After that, ZnO (20 nm) layer was deposited using the previous solution, and the sample was annealed at 100 °C for 60 s. A solution of PTB7:$PC_{71}BM$ was left idle for 1 h in a glovebox before to be spincaoted on the ZnO surface. Finally, a hole transport layer of MoO_3 (15 nm) deposited by spincoating and an anode of Ag (150 nm) was deposited using a thermal evaporator operating at ~5×10^{-6} Torr. The photoactive area of 18 mm^2 was achieved using a shadow mask. All steps were carried out inside N_2 -filled glovebox.

2.4. Device characterizations

The *J–V* curves were measured using a Keithley 2400 source measure unit (SMU) under illumination with an incident light intensity of 100 mW cm^{-2} (Atlas Solar constant 575PV AM 1.5 G light source) calibrated using a standard silicon reference cell (91150 V, Oriel Instruments). External quantum efficiency (EQE) spectra were obtained using an IPCE measurement system described previously. [40] The mismatch was calculated using standard procedure [41] of the J_{SC}