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Inverted ITO- and PEDOT:PSS-free polymer solar cells with high power conversion efficiency

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ABSTRACT

Highest published power conversion efficiencies of organic solar cells have mostly been achieved on substrates bearing a transparent indium tin oxide (ITO) electrode. However, the incorporation of ITO is not suited for future industrial production processes of organic solar cells, which will rely on a high-throughput of flexible substrates in order to achieve low cost of the final product. In this manuscript we present an alternative transparent electrode consisting of a layer stack of aluminum doped zinc oxide and a thin silver layer. Substrates with these electrodes have a transparency of above 75% in the wavelength range in which the photoactive layer absorbs light. Solar cells with a bulk-heterojunction of PTB7 and $PC_{71}BM$ in an inverted device architecture achieved a power conversion efficiency of 6.1%, which is the highest reported value for polymer solar cells free from both ITO and PEDOT:PSS. The sheet resistance of the novel electrodes increased only marginally after repeated bending which shows their full compatibility with future reel-to-reel processes or flexible products.

1. Introduction

The power conversion efficiency of organic solar cells has steadily been increased during the past years. While the barrier of 10% efficiency, which is regarded to be the lower limit for a successful commercialization of organic photovoltaic (OPV) devices [1–4], has already been broken for small molecule devices [5,6] and tandem solar cells employing polymers as photoactive materials [1,7], the published record efficiency for polymer single junction solar cells is 9.2% [3]. This record was set by employing the already semi-commercially available low-band gap polymer poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7) in an inverted device architecture, *i.e.*, the transparent indium tin oxide (ITO) electrode is turned into the electron collecting contact by surface modification with a conjugated polymer, poly[(9,9-bis(3′-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN). Polymers from the PTB family contain electron-pushing benzodithiophene units and electron withdrawing ester-substituted thienothiophene units, resulting in a small band gap of the molecules [8]. In a standard architecture, where the ITO electrode is coated with poly-(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) and used as a hole collecting electrode, an efficiency of 8.37% was reached using the same polymer [9]. The high efficiencies for PTB7 and other well-performing polymers in combination with fullerene derivatives [6,6]-phenyl-C_{61}- ($PC_{61}BM$) or [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) as electron acceptors were therefore realized in devices built on substrates bearing an ITO electrode [10–15]. ITO, however, has some shortcomings in connection with OPV devices. One major advantage of OPV devices, compared to other photovoltaic techniques, is the potential of their cheap production using a reel-to-reel process at low temperatures. Even if the final product might be intended to be rigid, flexible substrates are needed for this high throughput and thus low cost production process. ITO's brittle nature prevents it from being bent multiple times [16–20], rendering it as a nonideal candidate for these processes and difficult to process especially on flexible substrates. Furthermore, ITO is a scarce and thus expensive material, being considered to hold the highest share in material costs [21,22] as well as the highest share of energy input [23] in the production of ITO-based organic solar cells. For these reasons, several concepts for organic solar cells with ITO-free transparent electrodes have been developed, using printed or evaporated metal grids [24–31], highly conductive layers of poly(3,4-ethylene-dioxythiophene) (PEDOT) [32–38],

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other conductive polymers like polyaniline [39], carbon based materials like graphene or carbon nanotubes [40–46], metal nanowire layers [47–50], thin metal layers [51–56], alternative transparent conducting oxides [57–61] or a combination of some of these mentioned above [62,63]. Adding to this, our group has demonstrated a wrap-through concept for organic solar cells, in which both kinds of charge carriers are extracted at the cell's backside [25]. The highest reported power conversion efficiency of an ITO-free device is 6.56%, employing a low-band gap polymer on the top of a transparent layer stack of tellurium dioxide, silver and PEDOT:PSS [20]. The PEDOT:PSS buffer layer, however, can also have detrimental effects on OPV devices, as many of its solutions used for layer deposition are acidic in nature and can thus harm underlying acid sensitive metal oxide [64–66] and metal layers. While this might not be an issue for the record ITO-free device, where a neutral PEDOT:PSS solution has been deposited on the top of a silver layer, which is in any event resistant against non-oxidizing acids [67], PEDOT:PSS is also a hygroscopic material [65,68]. Thus, water penetration into the solar cell is facilitated when PEDOT:PSS is incorporated, which in turn has detrimental effects on the lifetime of the device [68–71].

In this paper, we present an alternative architecture for highly efficient, ITO- and PEDOT-free inverted polymer solar cells. A sputter-deposited stack of a thin silver (Ag) layer embedded between two layers of aluminum doped zinc oxide (AZO) serves as a transparent electron contact. On top of this, a bulk heterojunction of PTB7 and $PC_{71}BM$ is used as the photoactive layer. A thin layer of molybdenum trioxide and a silver mirror as the hole contact complete the cell (Fig. 1).

2. Material and methods

PTB7 (Lot YY3-293P) was purchased from 1-Material (Quebec, Canada), $PC_{71}BM$ (99%) from Solenne (Groningen, The Netherlands) and PEDOT:PSS (Clevios™ P VP AI 4083) from Heraeus Precious Metals (Leverkusen, Germany). Other chemicals and solvents were purchased from Sigma-Aldrich (St. Louis, MO, USA). ETL-1 was synthesized similar to a published procedure [72], but using toluene instead of chlorobenzene in the synthesis of the monofulleropyrrolidine and with a slightly different stoichiometry. For the fabrication of ITO-free solar cells, glass substrates were coated with a stack of AZO (25 nm), silver (9 nm) and another AZO-layer (20 nm) by DC magnetron sputtering. For the deposition of the AZO layers, a ceramic target containing 2% of aluminum was used. AZO was deposited at a power density of 2.7–2.8 W/cm^2 in an argon atmosphere with 10% and 1% O_2 for the first and second AZO-layer, respectively. A metallic silver target was used for the silver deposition at a power density of 0.7 W/cm^2 in a pure argon atmosphere. The pressure was adjusted to

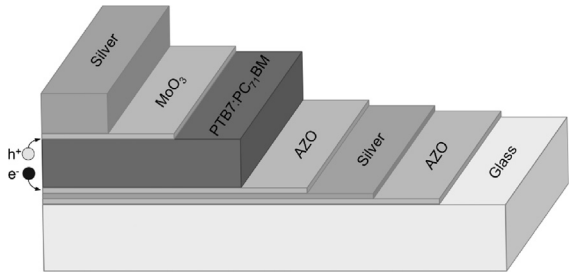

Fig. 1. Scheme of the inverted ITO-free cell architecture described in this paper. Illumination takes place through the glass substrate and the transparent electrode consisting of thin aluminum-doped zinc oxide (AZO) and silver layers. Holes (h^+, light circle) and electrons (e^-, dark circle) are extracted at the MoO_3 and AZO interfaces, respectively.

5×10^{-3} mbar in all cases. Shadow masks were used during the deposition process for patterning the substrates. The substrates were cleaned in a water bath under ultrasonic agitation for 5 min, blow dried with nitrogen and additionally dried in an oven at 100 °C for 10 min. All subsequent steps were performed in a system of interconnected, nitrogen filled gloveboxes. The photoactive layer was spin-coated onto the substrates from a PTB7/$PC_{71}BM$ solution in chlorobenzene containing 3% 1,8-diiodooctane. The resulting layer thickness was 90–100 nm as determined with a Dektak 150 surface profiler. A 10 nm layer of MoO_3 and a 100 nm layer of silver were thermally evaporated under vacuum to complete the layer stack. For the construction of reference devices, prepatterned ITO substrates were cleaned twice and subsequently in acetone, isopropanol and water under ultrasonic agitation for 5 min each, blow dried with nitrogen and UV–ozone treated for 20 min. A 40 nm thick PEDOT:PSS layer was spin-coated onto the substrates which were then annealed at 130 °C for 20 min. All subsequent steps have been performed under nitrogen atmosphere. The photoactive layer was spin-coated from the solution and with the parameters used in the construction of ITO-free devices. A thin layer of ETL-1 was spin coated on top of the photoactive layer, using a 1 mg/mL solution of ETL-1 in methanol and a rotational speed of 5000 rpm. The layer stack was completed by thermal evaporation of 100 nm aluminum acting as a mirror electrode. The active area of solar cells in both standard and inverted architecture was 0.09 cm^2. Current–voltage curves were measured using a Keithley 2400 source meter and under simulated AM1.5G illumination (1000 W/m²) corrected for spectral mismatch. Spectral measurements of PEDOT:PSS coated ITO substrates and uncoated AZO/Ag/AZO substrates were carried out on a Bruker IFS66 spectrometer equipped with an integrating sphere. Bending tests were performed using commercial ITO coated PET foil from Sigma-Aldrich with a listed sheet resistance of 60 Ω/sq and with a custom made AZO/Ag/AZO coated PE foil. The foils were repeatedly bent around a cylinder with 9 mm diameter and the sheet resistance was measured using a four-point-measurement setup, both along and perpendicular to the bending direction. Values given for the sheet resistance are the mean value of both measurements. Before and after the tests, optical microscopic images were taken using an Olympus Vanox-T AH-2 optical microscope and 20 × magnification.

3. Results and discussion

Before building solar cells, the AZO–silver–AZO substrates as well as the PEDOT:PSS-covered ITO-substrates used for the construction of reference devices were tested for their transparency and conductivity. The sheet resistance of the ITO-free electrodes was 9 Ω/sq, which is comparable to the sheet resistance of commercial ITO used in reference devices, which was 7 Ω/sq. The thickness of the ITO-layers, however, was higher (130 nm) than the one of the AZO/Ag/AZO layer stack (54 nm). The integrated transmission in the wavelength range of 320–800 nm, which covers the absorption range of PTB7:$PC_{71}BM$ blend layers, was 75.7%, peaking at 530 nm with 86% transmission. A higher transparency of 83.2% was observed for the PEDOT:PSS-covered ITO substrates in the same wavelength range, peaking at 500 nm with 89.2% transmission (Fig. 2). As can be seen from the spectra, the transmission of the ITO-free substrates is generally below that of the coated ITO substrates, which could result in a lower photocurrent of the ITO-free solar cells.

Organic solar cells were assembled both with the ITO-free architecture depicted in Fig. 1 and with a layer stack of glass/ITO/PEDOT:PSS/PTB7:$PC_{71}BM$/ETL-1/Al for comparison to an ITO-based device with standard architecture. ETL-1 (Fig. 3) is a methanol-soluble