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A rational method for developing and testing stable flexible indium- and vacuum-free multilayer tandem polymer solar cells comprising up to twelve roll processed layers

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ABSTRACT

We demonstrate a method for the preparation of multijunction polymer solar cells without the use of vacuum evaporation methods or indium tin oxide (ITO). The entire layer stack is prepared by printing or coating of each layer. The number of layers typically employed in complete devices exceeds ten and to efficiently identify layers and interfaces that are not robust we developed a double sided illumination method and demonstrate how layer thicknesses can be optimized with respect to the roll processing in the aim of achieving functional tandem devices. The devices were prepared directly on barrier foil and were later encapsulated. In this study the same active material comprising poly-3-hexylthiophene (P3HT) and phenyl-C_{61}-butyric acid methyl ester ([60]PCBM) was employed using nanoparticle based zinc oxide for electron selectivity and several different PEDOT:PSS formulations for hole selectivity, electrode- and recombination layer formation. A novel slanted comb silver grid electrode structure was employed to enable efficient double sided illumination and minimize shunts. The operational stability of the tandem devices evaluated under ISOS-D-2 conditions demonstrated less variation in stability between devices than similar single junctions prepared in the same manner for reference. We demonstrate lifetime studies for 480 h without any sign of degradation and estimate that the tandem or multijunction polymer solar cells are as stable as single junctions.

1. Introduction

The polymer tandem solar cell has been reviewed several times [1,2] and until now it has mostly been reported with a very small active area on rigid glass substrates using indium tin oxide (ITO) as the semitransparent front electrode and vacuum evaporated back metal back electrodes. In many cases the recombination layer has also been vacuum processed and thus only the two active layers have been solution processed. In some cases the recombination layer has been solution processed [1,2] but in the majority of cases most processing has been carried out in a glovebox and using vacuum deposition for many of the layers. The polymer tandem solar cell prepared without the use of semitransparent indium–tin-oxide electrodes and vacuum steps using only ambient conditions for roll-to-roll printing and coating on flexible substrates undoubtedly represents the ultimate challenge and the pinnacle of complexity within the field of printed and organic electronics [3]. It is also likely that all these requirements will be necessary before tandem polymer solar cells can become useful outside academic reports. The motivation for preparing the polymer tandem solar cell is clearly the desire to reach the highest achievable performance and the tandem approach or multi-junction approach to photovoltaics in general is the undisputed route to the highest performance in terms of power conversion efficiency. The tandem solar cell also presents the drawback of being more complicated with a significantly smaller room for error and the effort is only justified provided that the process is robust and the extra effort required for its making is returned as a higher efficiency at lower process intensity and a lower embodied energy. The increased complexity is quite possibly also the reason why tandem polymer solar cells initially did not attract so much attention compared to single junctions as shown in Fig. 1 where it is clear that the number of tandem solar cell publications did not increase significantly beyond 10 articles per year until 2010 [3]. In spite of this much lower number of publications by two orders of magnitude the tandem solar cell is rapidly approaching the best reported single junctions.

Printing and coating of polymer solar cells [4] has already been demonstrated to be a fast and viable approach to the manufacture of polymer solar cells while there has been a significant gap

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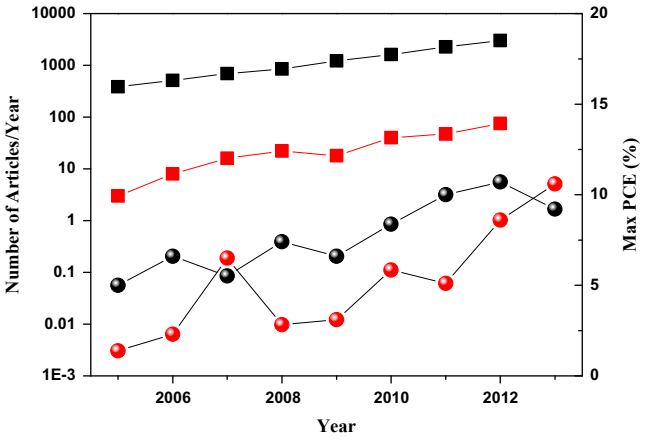

Fig. 1. The number of scientific reports on OPV as a function of time (black squares, left *y*-axis) as compared to the number of tandem solar cell reports (red squares, left *y*-axis) shown on a logarithmic scale. The maximum reported PCE (%) for each year for single junction cells (black spheres) and tandem cells (red spheres). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

between the reported record efficiencies for small laboratory cells and the well corroborated performance of large area polymer solar cell modules. In addition to this, early printed polymer solar cells still employed indium–tin-oxide as the semitransparent front electrode while several life cycle analysis studies showed that an alternative to indium based electrodes is mandatory for rational use of polymer solar cells including tandem polymer solar cells [5–8]. It was also established that vacuum processing steps require very high polymer solar cell performance to be justified and that printed or coated (vacuum free) polymer solar cells can reach much shorter energy payback times even with a lower performance [9]. While the justification for avoiding both vacuum and indium is compelling it has taken an enormous effort to find convincing alternatives due to the enormous complexity of printing and coating thin 2-dimensionally patterned multilayer films. Traditional processing has limited the number of wet coating steps and has employed vacuum processing wherever possible and this has elegantly avoided the unforgiving challenge of interfacing many thin layers without shunting. Recently a very efficient low cost flexible semitransparent electrode was developed which is in fact so cheap to process that it is freely available to academics [10]. This electrode and processing philosophy serves as the foundation in this work and is explored for processing of tandem polymer solar cells. The largest challenge for the tandem solar cell is how the thicknesses of the individual layers critically influence the overall device performance and imposes firm requirements on the processing conditions as subsequently processed layers must not adversely affect or change previously processed layers. This can to a certain extent be solved through vacuum processing of some layers such as the electrodes and oxide layers. The industrially relevant processes are however expected to employ only printing and coating which does represent a very challenging task and the successful development of functional tandem devices following that approach does require a novel protocol that enables fine tuning of the individual junctions and the interlayers such that a functional device is guaranteed during development even if the given device does not represent the optimal choice. There are two points that must be rationally addressed to achieve this, the first point is that one must be able to address the individual junctions optically such that their individual performance can be established and optimized and the second point is the optimization of the processing conditions for the secondly processed junction such that the performance of the first junction is not adversely affected. We have in the past successfully prepared tandem solar cells through use of thermocleavable materials [11] whereby the active layers and the interlayers are insolubilized after processing thus enabling solution processing of subsequent layers without affecting underlying layers. The performance was however relatively poor for this approach and required temperature stable glass substrates. In a second embodiment full roll-to-roll processing was employed in all layers on flexible ITO substrates by use of water based emulsions for the back junction [12]. The performance was also found to be poor in this case as the devices had a large active area.

In this work we present our approach to optimize fully printed and coated flexible tandem polymer solar cells and we successfully demonstrate how this method allows for establishing the process windows for new materials combinations in multilayer tandem polymer solar cells. The use of organic solvent based inks was deemed necessary and an optimization of the intermediate layer towards a higher degree of solvent resistance was achieved. For testing of the device performance, and in particular the efficiency of the intermediate layers, a specialized illumination geometry was developed where the device is illuminated from both sides thus enabling controlling the incident light intensity on each junction.

2. Experimental

Solar cells were manufactured on a barrier material substrate (Amcor) with a silver grid/conductive PEDOT:PSS/ZnO electrode. This ITO-free semitransparent electron accepting front electrode known as Flextrode has been previously described [10] and can be obtained freely at www.plasticphotovoltaics.org. Cells were prepared directly on the Flextrode and consisted of a fully slot-die coated layer stack. The final metal back electrode was printed using the flexo technique. The machinery employed has been described [13,14]. ZnO was employed as an electron transport layer, P3HT:PCBM as the active layer, the intermediate recombination layer with a compatibilizing layer comprising PEDOT:PSS and ZnO.

2.1. Materials

Poly-3-hexylthiophene (P3HT from Plextronics) had a M_n of 40.000 Da. Phenyl-C_{61}-butyric acid methyl ester ([60]PCBM, from Solenne) had a purity of 99%. The P3HT:[60]PCBM ink used was 20:20 mg mL^{-1} ink dissolved in chlorobenzene with 10% chloroform and 3% chloronaphtalene, for 100 nm thick active layer a 10:10 mg mL^{-1} solution was used for coating. Electron transport layers (ETL) were coated using a stabilized ZnO nanoparticle solution in acetone (49 mg/mL). Several hole transport layers (HTL) were employed in the process of optimizing the method. V_2O_5 was employed where stated as a HTL and compatibilizer layer between the first active layer and the poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) layer and comprised of a vanadium(V)oxiiso-propoxide:isopropanol (IPA) (1:100; 1:1000; 1:2000) solution. Several PEDOT:PSS HTL formulations were used; Clevious P VP Al 4083 or Clevios F-010. In the case of AL 4083 PEDOT:PSS it was mixed in a ratio of 1:2 with IPA and 2% ethyl glycol. PEDOT:PSS (Clevios F-010) was diluted 7:3 with IPA to enhance wetting properties. A MoO_x precursor solution in isopropanol was employed as a second HTL and/or compatibilizer where stated from a neutralized IPA solution. The printable silver back electrode used was PV410 from Dupont. The substrate used was Flextrode with a honeycomb (as described in Ref. [10]) or line silver pattern as developed in this work (see Fig. 2). The cells were encapsulated between two 18 × 18 mm^2 glass slides with