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## Double and triple junction polymer solar cells processed from solution

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Multiple junction solar cells incorporating polymer:fullerene bulk heterojunctions as active layers and solution processed electron and hole transport layers are presented. The recombination layer, deposited between the active layers, is fabricated by spin coating ZnO nanoparticles from acetone, followed by spin coating neutral pH poly(3,4-ethylenedioxythiophene) from water and short UV illumination of the completed device. The key advantage of this procedure is that each step does not affect the integrity of previously deposited layers. The open-circuit voltage ( $V_{oc}$ ) for double and triple junction solar cells is close to the sum of the  $V_{oc}$ 's of individual cells. © 2007 American Institute of Physics. [DOI: 10.1063/1.2719668]

Solar cells based on organic and polymer materials have the potential advantages of low cost and light weight compared with traditional solar cells.<sup>1–3</sup> However, organic solar cells have not yet reached the level of practical use due to their lower efficiency compared to, e.g., silicon-based devices. One possible way to improve the efficiency is by using a tandem configuration in which two or more cells with different absorption spectra, i.e., different band gaps, are stacked. This increases the absorption of solar light and allows utilizing the photon energy more efficiently. In a two terminal tandem cell, with the active layers connected in series, the open-circuit voltage ( $V_{oc}$ ) is the sum of the  $V_{oc}$ 's of the subcells.

In order to construct an organic or polymer tandem solar cell, a transparent intermediate layer positioned between the two active layers is required, which provides electrical contact between the two cells via efficient recombination of the holes and electrons created in the different subcells without voltage loss. Preferably, the intermediate layer consists of a nonabsorbing electron transporting layer (ETL) in contact with the front cell and a hole transporting layer (HTL) in contact with the back cell. Organic tandem solar cells based on small molecules have been described and indeed show increased open-circuit voltage and efficiencies.<sup>4–10</sup> Also, solution processed organic tandem solar cells with evaporated or sputtered intermediate layers have been reported.<sup>11,12</sup> Solution processed ETLs and HTLs, however, are more interesting because spin (or blade) coating and ink-jet printing are techniques which are less time and energy consuming and are on the way to roll-to-roll production.<sup>13,14</sup> While an example of an intermediate layer processed from solution was reported recently,<sup>15</sup> efficient solution processed ETLs and HTLs are required to make efficient multiple junction solar cells. The main difficulty, so far, has been creating this multiple layer structure without dissolving or destroying the underlying layers.

In this letter, we present a straightforward and versatile solution-based method to process electron and hole transport layers consisting of ZnO nanoparticles and poly(3,4-ethylenedioxythiophene) (PEDOT), respectively. Importantly, we have established a solvent combination that allows

subsequent layers to be processed without affecting previously deposited layers. To demonstrate the technique, we use well-established material combinations for the active layers, employing blends of poly(3-hexylthiophene) (P3HT) and poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-*p*-phenylene vinylene] (MDMO-PPV) as electron donors mixed with a soluble fullerene derivative [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) as electron acceptor.<sup>16–19</sup> We show that the method is fast, easy, and applicable to multiple junction solar cells. In the future, the intermediate layer can be used to combine materials with different band gaps to have an increased coverage of the solar spectrum.

Our device structure for a tandem solar cell with the intermediate layers processed from solution is shown in Fig. 1. For fabrication of the devices, cleaned indium tin oxide (ITO) patterned glass substrates (Philips Research) were covered by spin coating a poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) dispersion (Baytron® P VP AI 4083; H.C. Starck) after filtration using a 0.45  $\mu\text{m}$  filter. For the active layers, P3HT (Rieke Metals), MDMO-PPV, and PCBM (Solenne BV) were used. The thin films of a blend of MDMO-PPV:PCBM with a weight ratio of 1:4 were spin coated from a 3 mg/ml chlorobenzene solution and thin films of a blend of P3HT:PCBM with a weight ratio of 1:1 were spin coated from a 10 mg/ml chlorobenzene solution.

To spin coat a new layer on top of the active polymer:fullerene layer, the solvent used should not disturb the underlying layer. We found that acetone is one of the few solvents that is innocuous to the organic active layer. For the ETL, ZnO nanoparticles were used and prepared as described previously,<sup>20,21</sup> dissolved in acetone (15 mg/ml), and

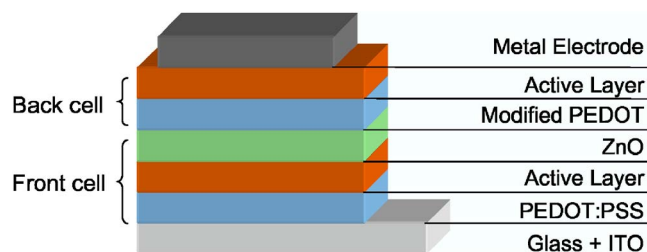


FIG. 1. (Color online) Device setup for a solution processed tandem solar cell.

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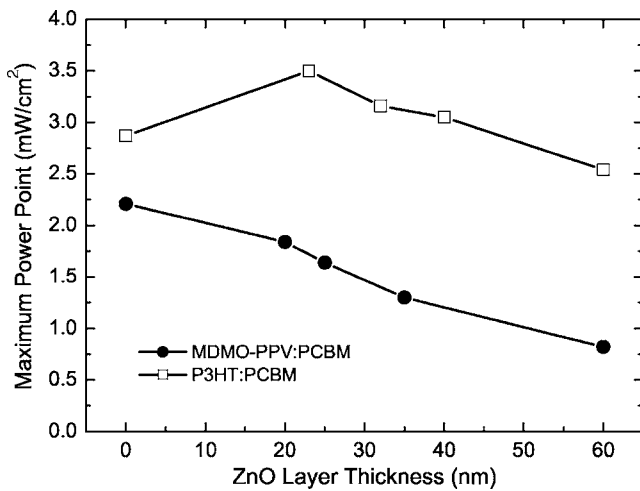


FIG. 2. Effect of a ZnO layer sandwiched between the active layer and the LiF/Al electrode for P3HT:PCBM and MDMO-PPV:PCBM solar cells. The active layers were 80 nm thick.

deposited by spin coating to obtain a 30 nm thick layer. To determine the quality of the ZnO as ETL, devices with the ZnO layer sandwiched between the active layer and a LiF/Al top electrode were made. Working devices were obtained for different ZnO layer thicknesses and active layer combinations, demonstrating that these ZnO nanoparticle layers can be used as ETL in tandem cells. P3HT:PCBM solar cells with a thin ZnO layer show even an increase in current and maximum power point (Fig. 2). Similar effects have been described using a sol-gel processed  $\text{TiO}_x$  layer.<sup>22</sup>

The acidic Baytron® P dispersion of PEDOT:PSS in water could not be used to deposit the HTL onto this ETL because it dissolves ZnO. Therefore we used a modified PEDOT dispersion at neutral pH (Orgacon, batch 5541073, pH=7, 1.2 wt %, Agfa Gevaert NV), which was spin coated from water after 1:1 dilution to obtain a 15 nm layer. Subsequently, the second active layer was deposited via the same procedure as used for the first layer. All layers could be de-

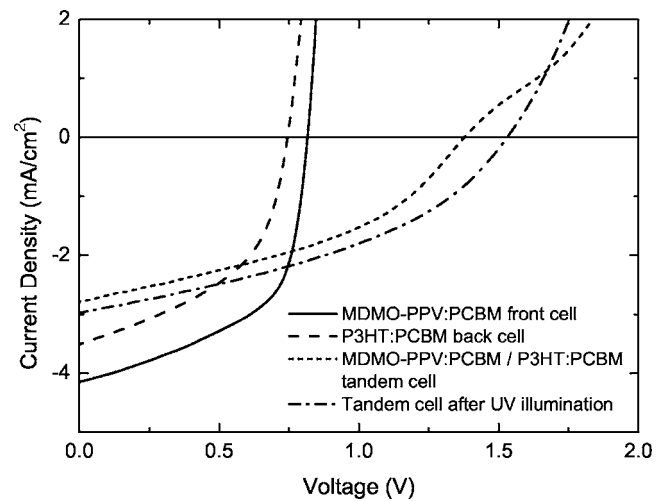


FIG. 3. Current density–voltage characteristics of the front, back, and tandem cells under an arbitrary halogen lamp. Notice the improved performance after UV illumination.

posited on top of each other without disrupting the underlying layers.

After completion of the solution processing of the various layers, the samples were moved into a glovebox with a nitrogen atmosphere to evaporate 1 nm of LiF and 100 nm of Al as the top electrode at  $10^{-5}$  mbar. Current-voltage characteristics were measured with a Keithley 2400 source measurement unit. Illumination was carried out with UV (GG 385) and infrared (KG1) filtered light from an uncalibrated tungsten halogen lamp ( $75 \text{ mW/cm}^2$ ). The light intensity of this light source provides for MDMO-PPV:PCBM and P3HT:PCBM blends a power output that is within 20% of the AM1.5 ( $100 \text{ mW/cm}^2$ ) performance. UV illumination was performed with the same halogen lamp, however, without the GG 385 filter. Layer thicknesses were determined with a Tencor® P-10 surface profiler.

The transparent ZnO/PEDOT recombination layer was tested in tandem solar cells with MDMO-PPV:PCBM and

TABLE I. Solar cell characteristics of multiple junction organic solar cells with ITO/PEDOT:PSS as transparent electrode, ZnO/modified PEDOT as intermediate layer, and LiF/Al as reflective electrode. All cells are polymer:PCBM cells. The front and middle cells have an ITO/PEDOT/active layer/ZnO/metal structure.  $V_{\text{est}}$  is the estimated value for the voltage for a multiple junction cell obtained via superposition of the voltages of the single junction cells.

Front cell (45 nm)	Middle cell (65 nm)	Back cell (85 nm)	UV	$V_{\text{est}}$ (V)	$V_{\text{oc}}$ (V)	$I_{\text{sc}}$ ( $\text{mA/cm}^2$ )	FF (%)	MRP ( $\text{mW/cm}^2$ )
MDMO-PPV	...	...			0.82	4.1	55	1.9
...	MDMO-PPV	...			0.82	4.4	55	2.0
...	...	MDMO-PPV			0.82	4.9	57	2.3
...	...	P3HT			0.75	3.5	48	1.3
MDMO-PPV	...	MDMO-PPV	No	1.64	1.34	2.7	37	1.3
			Yes		1.53	3.0	40	1.8
MDMO-PPV	MDMO-PPV	MDMO-PPV	No	2.46	1.40	1.9	34	0.9
			Yes		1.92	2.4	33	1.5
MDMO-PPV	...	P3HT	No	1.57	1.38	2.8	40	1.6
			Yes		1.53	3.0	42	1.9
MDMO-PPV	MDMO-PPV	P3HT	No	2.39	1.71	2.2	36	1.4
			Yes		2.19	2.6	37	2.1

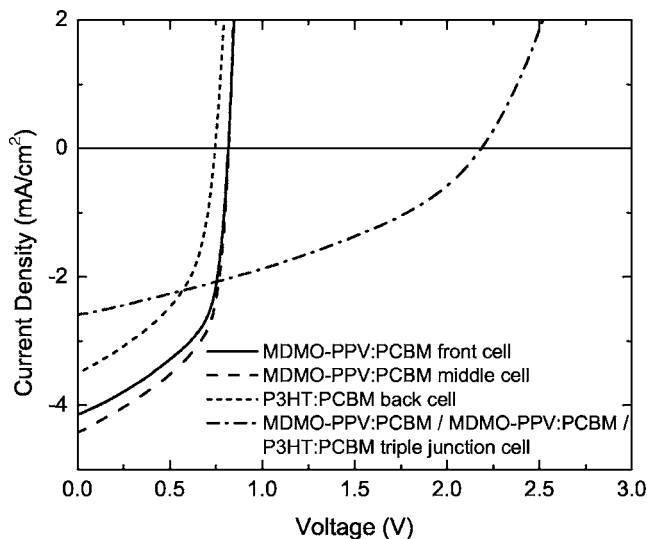


FIG. 4. Current density–voltage characteristics of the front, middle, and back cells and of the resulting triple junction cell after UV illumination.

P3HT:PCBM blends as active layers. For a tandem cell with MDMO-PPV:PCBM as front cell and P3HT:PCBM as back cell, an increase in  $V_{oc}$  from 0.75–0.84 to 1.34–1.38 V was obtained (Fig. 3 and Table I). This voltage, however, is not the sum of the voltages of the two single junction cells. We attribute this to a non-Ohmic contact between the ZnO and the modified PEDOT layers. This  $p$ - $n$  junction acts as a counterdiode, which causes a small voltage drop and results in an s-shaped  $I$ - $V$  curve (Fig. 3). Recombination across this interface can be improved by the introduction of an extremely thin metal film.<sup>6</sup> When 1 nm of silver is evaporated onto the ZnO before depositing the modified PEDOT, the inflection point in the  $I$ - $V$  curve disappears and  $V_{oc}$  increases to 1.49 V. Alternatively, an Ohmic contact between ZnO and PEDOT can also be obtained by sufficient doping of the two materials. PEDOT is already heavily doped and ZnO can very easily be doped by exposure to UV irradiation.<sup>21,23</sup> After a few seconds of UV illumination, the shape of the  $I$ - $V$  improves and  $V_{oc}$  increases to 1.53 V. Moreover, due to the increased conductivity of the doped ZnO layer, the short-circuit current ( $I_{sc}$ ) also increases, resulting in an overall 50% improvement of the maximum power point (Fig. 3).

In a similar fashion, multiple junction solar cells with three active layers were processed within 10 min, excluding metal evaporation, and an  $V_{oc}$  of 1.71 V was obtained. After UV illumination, the  $V_{oc}$  even increased to 2.19 V. Results are shown in Fig. 4 and Table I. The  $I$ - $V$  characteristics of the front, middle, and back cells are measured from a single junction cell with the same layer thickness and the same top and bottom contacts as in a multiple junction structure. The layer thicknesses are increased from front to back cells to permit sufficient light transmission to the back cell in order to have a decent current matching. The overall current for a two terminal device with the active layers in series is the lowest of all individual cells.

In conclusion, we fabricated organic multiple junction solar cells by solution processing using a recombination layer composed of ZnO nanoparticles and  $pH$  neutral PEDOT. Besides evaporation of the final metal back electrode, no other techniques than spin coating were required. Device efficiency improved by 50% with UV illumination due to photodoping of ZnO. An  $V_{oc}$  of 2.19 V was achieved for a triple junction solar cell, corresponding closely to the sum of single cell  $V_{oc}$ 's. This simple procedure to create multijunction devices will enable increasing the overall efficiency when active materials with different optical band gaps are used.

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