# Unconventional device concepts for polymer solar cells

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ABSTRACT: The inclusion of metal-oxide layers in polymer solar cells enables the fabrication of a series of unconventional device architectures. These devices include: semi-transparent polymer solar cells, devices with inverted polarity, as well as devices with air stable electrodes. A proof-of-principle of these devices is presented. The anticipated benefits of these novel device structures over conventional polymer solar cells are discussed.
Keywords: Organic solar cell, Polymer film, $TiO_2$, ZnO

## 1 INTRODUCTION

One of the anticipated attractive features of flexible polymer solar cells is the high production speed. One can use conventional roll-to-roll deposition technologies to deposit an ink containing a polymer:fullerene mixture, on to a suitable substrate. Investigated roll-to-roll deposition technologies include printing technologies, for example inkjet, gravure and flexo-graphic, and coating technologies such as curtain and slot die coating. These deposition techniques enable production speeds in the order of square meters per second.

In a conventional polymer solar cell (see Scheme 1), the photoactive layer, consisting of the polymer:fullerene blend, is sandwiched between two asymmetric electrodes. The hole collecting electrode is formed by an ITO layer, coated with PEDOT:PSS, whereas the electron collecting electrode is a low workfunction metal such as Ca, Ba or LiF/Al.

It is a challenge to fabricate this complete layer stack with roll-to-roll deposition technologies at a high speed against low cost.

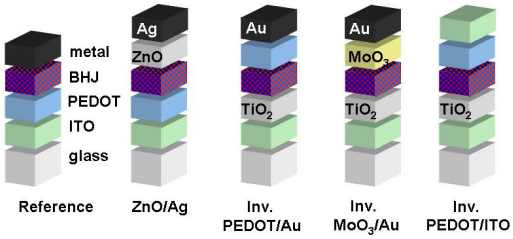
## 2 EXPERIMENTAL

An overview of the devices is depicted in scheme 1. Below a description is given how these structures were prepared and evaluated.

### 2.1 Conventional devices (Reference)

Glass substrates were used with pre-patterned ITO electrodes (Naranjo substrates). The substrates were carefully cleaned, dried, and treated with $UV/O_3$ prior to use. On the substrates, a 40 nm thick layer of PEDOT:PSS (Clevios Al 4083, H.C. Starck) was spin coated. Samples were subsequently dried for 10 minutes at 120°C.

The P3HT:[C60]PCBM layer was formed by spin coating an ortho-dichlorobenzene solution containing the P3HT (Plexcore OS2100, Plextronics):[C60]PCBM (99.5%, Solenne B.V.) mixture in a weight ratio of 1:1. Several different solutions were prepared with weight ratios in the range of 1.25 to 2.0 wt % of P3HT. The spin-coating conditions were adjusted to give photoactive layers with the desired thickness. Samples were annealed at 120°C for 5-10 min.




**Scheme 1:** Overview of the layer stack of the different device configurations. 'BHJ' abbreviates for bulk heterojunction; 'Inv.' for a device with an inverted polarity as compared to the reference device.

Devices containing the Plexcore PV2000 system (Plextronics), were processed in a similar way. After spin coating and annealing the PEDOT:PSS (Clevios Al 4083, H.C. Starck) layer, the PV2000 ink was spin coated. The sample was subsequently annealed at 170°C for 10 minutes. Note, the PV2000 ink system contains two inks. In the samples reported here, only the ink for the photoactive layer is used.

The devices were completed by vacuum deposition of the counter electrode. For P3HT:[C60]PCBM devices, the counter electrode was formed by a 1 nm layer of LiF and 80 nm of Al. For devices with the PV2000 system, the electron collecting electrode consists of 5 nm of Ca and 100 nm of Al. The electrode layers were vacuum deposited at $1\times10^{-6}$ mbar through a shadow mask. In this way, 4 cells were obtained with areas of 0.10 $cm^2$, 0.17 $cm^2$, 0.37 $cm^2$, and 1.0 $cm^2$ on the same substrate.

### 2.2 ZnO/Ag device

For devices with a ZnO/Ag electron collecting electrode, we used ZnO nanoparticles dispersed in acetone as described elsewhere.[1,2] The ZnO dispersion (~10 mg/ml in acetone) was spin coated on top of the P3HT:[C60]PCBM layer. The layer thickness of the ZnO layer was estimated to be 20-40 nm. For this measurement a surface profilometer was used, see below.

The Ag electrode was vacuum deposited in the same manner as the Al layer described above.

### 2.3 Device with inverted polarity (Inv. PEDOT/Au & Inv. $MoO_3$/Au)

The photoactive layer of inverted devices was either P3HT:[C60]PCBM or Plexcore PV2000. These layers were processed as described above.

The inversion of the polarity of the device implies an exchange of the electron and hole collecting electrodes.

As electron collecting contact we used ITO/$TiO_2$. The $TiO_2$ is deposited by manual or automated spray coating of a $TiO_2$ precursor. The precursor solution consists of titanium (IV) isopropoxide and acetylacetone in ethanol. During the spray process, the substrates lay on a hot plate at 460°C. After this spray step, substrates are sintered in an oven at 570°C for 30 minutes.

The hole collecting electrode of the inverted devices is formed by applying (spin coating or doctor blading) PEDOT:PSS on top of the photoactive layer. Typically wetting problems occur when depositing the hydrophilic PEDOT:PSS suspension on the hydrophobic photoactive layer. To overcome wetting issues, two different approaches were followed.

For the inverted devices with the PV2000 active layer, a viscous PEDOT:PSS formulation (Clevios S V3, H.C. Starck) was applied using doctor blading. In another approach we replaced the PEDOT:PSS by 10 nm thick, vacuum deposited $MoO_3$ or $Mo_3O_9$ layer.[3,4] The $MoO_3$ (99.9%, Sigma-Aldrich) is thermally evaporated from a boron nitride crucible (Kurt Lesker) at $1\times10^{-6}$ mbar. Both the PEDOT:PSS and $MoO_3$ layers are contacted with a thermally evaporated Au layer.

2.4 Semi-transparent device (Inv. PEDOT/ITO)

For semi-transparent polymer solar cells the same layer stack was applied as for devices with an inverted polarity described above. The thermally evaporated Au layer was replaced by a sputter deposited ITO layer with a thickness of 80 nm and a sheet resistance of 50 Ohm square.

2.5 Characterization

Film thickness measurements were performed with a Dektak 8 surface profilometer (Veeco).

Current-voltage (I/V) measurements were done in a setup (MiniSunSim) of our own design, containing a Keithley 2400 SourceMeter wired to a sample holder in a nitrogen-filled glove box. The sample was illuminated by a halogen lamp. An automated rotating filter wheel was used to record the current densities at various wavelengths for external quantum efficiency (EQE) measurement. A silicon reference cell with known spectral response was used for calibration purposes. This enabled the measurement program on the computer to calculate an estimation of the short-circuit current of the organic solar cell under 1000 W/m$^2$, AM1.5 illumination ($J_{sc,SR}$). Using this calculated short circuit current we estimated the power conversion efficiency (PCE) by: est. $PCE = V_{oc}$ (V) *$FF$* $J_{sc,SR}$ (mA/cm$^2$). For most measurements, the calculated short circuit current from the EQE measurement was within 10% of the measured short circuit current.

For standard test condition (STC) measurements, a WXS-300S-50 solar simulator (WACOM Electric Co.) was used. The mismatch factor (for these measurements, 0.96< mismatch factor <1) was calculated using a recent spectrum of the simulator lamp and the spectral responses of the used filtered Si reference cell (calibrated at the Fraunhofer ISE, Freiburg) and the polymer:fullerene cell, respectively.

Samples were illuminated through an illumination mask with a well defined aperture area.

3 RESULTS

3.1 Conventional devices

Conventional device structures are very useful for material engineering. Samples are routinely made and obtained results are often reproducible. Here we tested the commercial ink system PV2000 (Plextronics) and compared the results with a reference device containing a blend of P3HT:[C60]PCBM in a weight ratio of 1:1.

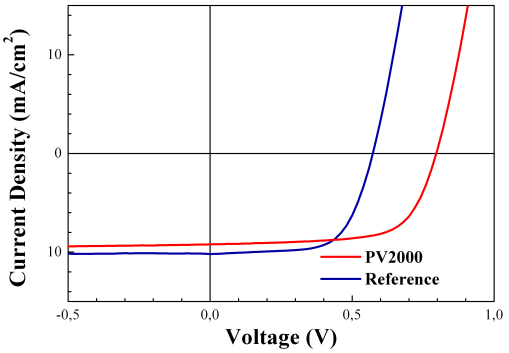



**Figure 1:** Current-density versus voltage curves of polymer solar cells with the PV2000 ink (red curve) and a reference device contains a P3HT:[C60]PCBM layer (blue curve). Both devices were made with the standard layer configuration.

From Fig. 1 it is clear that the improved performance of the device based on the commercial PV2000 ink is mainly caused by a significantly higher $V_{oc}$, as compared to the reference device. Table 1 summarizes the *JV*-characteristics of the device presented in Fig. 1.

In general, the $V_{oc}$ of a polymer solar cell is related to the energy difference between the ionization potential of the donor material (typically a polymer) and the electron affinity of the acceptor material (often a fullerene). The high $V_{oc}$ is therefore a strong indication that the energy levels of the PV2000 system differ from the energy levels of P3HT:[C60]PCBM.

The power conversion efficiency (PCE) of the PV2000 based device is 5.0 %.

**Table 1:** Overview of the *JV*-characteristics of devices with a standard layer stack. The reference device is made with P3HT:[C60]PCBM, the sample device is made with the PV2000 ink.

| Setup<br>**Sample**<br>(aperture [cm$^2$]) | MiniSunSim<br>**Reference**<br>(0.16) | WACOM<br>**PV2000**<br>(0.25) |
|---|---|---|
| $V_{oc}$ [mV] | 573 | 796 |
| $J_{sc}$ [mA/cm$^2$] | 10.2 | 9.4 |
| *FF* [%] | 65 | 67 |
| *MPP* [mW/cm]<br>(est.) *PCE* [%] | 3.8<br>(3.8) | 5.0 |

One of the disadvantages of the standard device configuration is the use of low workfunction metals like Ca or Ba to make a good electron collecting electrode. These metals are very sensitive to oxidation reactions. If the low workfunction metal becomes oxidized, a thin insulating layer is formed deteriorating the device performance. Below several device structures are presented which make use of (air) stable materials.

3.2 ZnO/Ag device

ZnO is an interesting candidate to be used in an air stable electron collecting electrode. ZnO can act as an efficient electron donor material. In fact, polymer based

bulk heterojunctions have been prepared using ZnO as electron collecting material.[2]

The ZnO layer can be formed by a variety of methods that are easy to operate in large area deposition processes.[1,2] Here we applied ZnO naoparticles, dispersed in acetone, using a recipe developed by Beek et al.[2] Smooth ZnO films were obtained with layer thicknesses of approximately 20-40 nm. The devices are completed by thermally evaporating an Ag contact. The result is presented in Fig. 2 and summarized in Table 2.

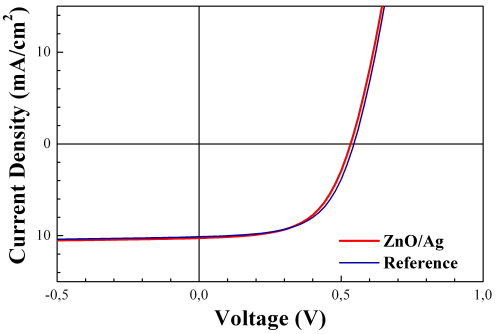



**Figure 2:** Current-density versus voltage curves of a polymer solar cell with a ZnO/Ag electron collecting electrode (red curve). In this device as well as the reference device (blue curve) the bulk heterojunction is formed by a P3HT:[C60]PCBM layer.

The current-density versus voltage curves of the reference and ZnO/Ag sample are nearly identical. Clearly, the application of the ZnO layer does not reduce the device performance. The fact that the ZnO layer is solution processed may be an additional advantage of this device concept as it is more compatible with high speed roll-to-roll processing.

Besides advantages in terms of stability and processability, the introduction of the ZnO layer may also increase the device performance. The ZnO layer may act as an electron transport/hole blocking and exciton separating layer. In addition, it provides an additional parameter to tune the optical field distribution of the photo active layer.[5]

**Table 2:** Summary of the *JV*-characteristics of devices presented in figure 2.

| Setup **sample** (aperture [cm$^2$]) | MiniSunSim **Reference** (0.09) | MiniSunSim **ZnO/Ag** (0.09) |
|---|---|---|
| $V_{oc}$ [mV] | 545 | 533 |
| $J_{sc}$ [mA/cm$^2$] | 10.1 | 10.3 |
| *FF* [%] | 58 | 57 |
| *MPP* [mW/cm] (est.) *PCE* [%] | 3.2 (3.3) | 3.1 (2.9) |

3.3 Device with inverted polarity

In another approach to develop polymer solar cells with air stable contacts, devices with inverted polarity were investigated. In these devices, the electrons are collected from the TCO side of the device while the holes are collected by the reflective metal at the rear side of the device.

Figure 3 compares the current-density versus voltage curves of a standard device based on the PV2000 system, with an 'inverted' device containing the same photoactive layer. Although the J/V curves are not identical, very similar device performances are obtained, see table 3. The inverted device compensates the lower fill factor with a higher short circuit current. It should be noted here that these devices were not completely optimized.

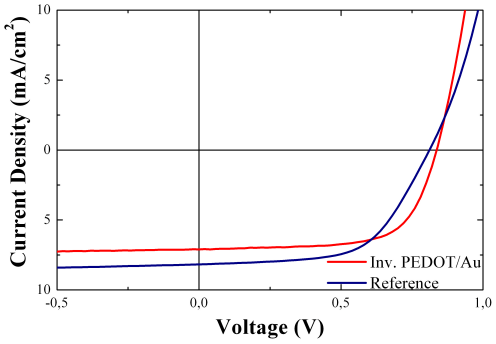



**Figure 3:** Current-density versus voltage curves of a polymer solar cell with an inverted polarity (red curve) as compared to a reference device (blue curve). In both devices, the bulk heterojunction is formed by the PV2000 system. The top electrode of the inverted device consists of a PEDOT:PSS layer covered with a gold layer.

The relatively high short circuit current of the inverted device is tentatively attributed to differences in the optical system. Also in this device configuration, the photoactive layer is sandwiched between two (nearly) transparent charge collection layers (here $TiO_2$ and PEDOT). In addition, similarly to ZnO, $TiO_2$ may act as an electron accepting material and may contribute to exciton dissociation.[7]

In short, the main benefit of this layer configuration is the possibility to use air stable materials as charge collection layers. Secondly, it may be easier to optimize the layer stack to improve light management. However, in terms of processability, this concept is less favorable.

**Table 3:** Summary of the *JV*-characteristics of devices presented in figure 3.

| Setup **sample** (aperture [cm$^2$]) | WACOM **Reference** (0.03) | WACOM **Inv. PEDOT/Au** (0.03) |
|---|---|---|
| $V_{oc}$ [mV] | 811 | 837 |
| $J_{sc}$ [mA/cm$^2$] | 8.2 | 7.1 |
| *FF* [%] | 59 | 67 |
| *PCE* [%] | 4.0 | 4.0 |

From Scheme 1 it is clear that the PEDOT:PSS layer should be stacked on the bulk heterojunction. This is in general a difficult task as the bulk heterojunction has hydrophobic surface whereas the PEDOT:PSS suspension is hydrophilic. It may not come as a surprise that wetting problems often occur during the preparation of these devices.

For the device presented in Figs. 3 and 5, the wetting problem was solved by applying a thick viscous PEDOT:PSS formulation using doctor blading. This layer was subsequently quickly dried at 170°C, to prevent dewetting.

Another method to overcome the dewetting problem

is to use of $MoO_3$ to replace PEDOT. The $MoO_3$ is deposited on the polymer:fullerene layer by vacuum deposition. The current-density versus voltage curve of an inverted device with a $MoO_3$ layer is depicted in Fig. 4.

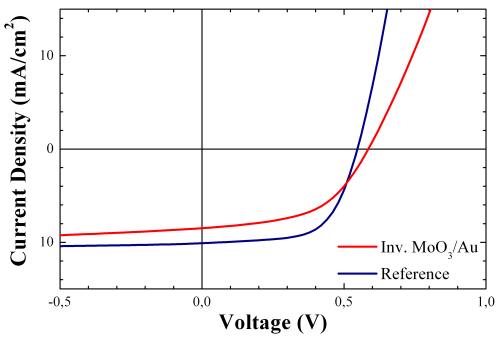



**Figure 4:** Current-density versus voltage curves of a polymer solar cell with an inverted polarity (red curve) as compared to a reference device (blue curve). In both devices, the bulk heterojunction is formed by the PV2000 system. The top electrode of the inverted device consists of a $MoO_3$ layer covered with an Au layer.

The performance of the inverted device with the $MoO_3$ layer to replace PEDOT:PSS is significantly lower as the reference device. This is at least partially caused by the low fill factor of the device. It is not completely clear what caused the low fill factor. Possibly it is caused by the semi automated $TiO_2$ sinter step used in this experiment. During the $TiO_2$ spray deposition, the sample is kept at 450°C. Depending on the exact processing conditions, the sheet resistance of the ITO may increase by a factor of 5 to 8 during this sinter step. Replacing $TiO_2$ by ZnO could solve this issue.

In addition to the advantages of the previously discussed inverted device (stable electrodes and light management), $MoO_3$ based inverted devices are easily processed under laboratory conditions. Nevertheless, it would be strongly preferred if the vacuum process could be replaced by a solution process. Yang Yang published recently on inverted devices based on solution processable $V_2O_5$.[6] It may also be possible to formulate a PEDOT solution with a reasonable wetting envelope.

**Table 4:** Summary of the *JV*-characteristics of devices presented in figure 4.

| Setup **sample** (aperture [cm²]) | MiniSunSim **Reference** (0.09) | MiniSunSim **Inv. $MoO_3$/Au** (0.03) |
|---|---|---|
| $V_{oc}$ [mV] | 547 | 586 |
| $J_{sc}$ [mA/cm²] | 10,1 | 8.5 |
| *FF* [%] | 62 | 52 |
| *MPP* [mW/cm] (est.) *PCE* [%] | 3.5 (3.2) | 2.6 (2.9) |

3.4 Semi-transparent device

By replacing the PEDOT/Au electrode of the inverted device discussed above, by a PEDOT/ITO electrode, it is possible to prepare a semi-transparent polymer based photovoltaic device. We used a low temperature ITO sputter technique to deposit ITO on the PEDOT layer. The device characteristics are presented in Fig. 5 and Table 5.

When compared to the reference device, the short-circuit current of the semi-transparent device is lower. This is also expected for a semi-transparent device. The other JV parameters presented in table 5 are very similar to the reference device.

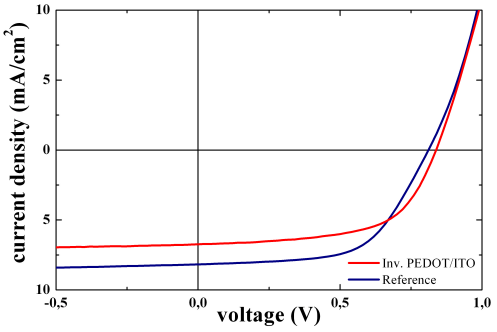



**Figure 5:** Current-density versus voltage curves of a polymer solar cell with an inverted polarity (red curve) as compared to a reference device (blue curve). In both devices, the bulk heterojunction is formed by the PV2000 system. The top electrode of the inverted device consists of a PEDOT layer covered with an ITO layer.

This device has very interesting features. The device performance is reasonable and may be further optimized.[8] The device contains air stable electrodes and has the additional benefit of being semi-transparent.
A disadvantage may be the fact that the ITO deposition is a vacuum step.

**Table 5:** Summary of the *JV*-characteristics of devices presented in figure 5.

| Setup **sample** (aperture [cm²]) | WACOM **Reference** (0.03) | WACOM **Inv. PEDOT/ITO** (0.03) |
|---|---|---|
| $V_{oc}$ [mV] | 811 | 838 |
| $J_{sc}$ [mA/cm²] | 8.2 | 6.7 |
| *FF* [%] | 59 | 60 |
| *PCE* [%] | 4.0 | 3.4 |

## 4. CONCLUSIONS

The application of metal-oxide layers in polymer solar cells enables the fabrication of a series of unconventional devices. A proof-of-principle of 4 of these devices is presented. The devices have anticipated advantages over the conventional layer stack. These benefits include air stable electrodes, device manufacturability and semi-transparent electrodes. All these devices gave reasonable device performances in the range of 2.9 - 4.0%.

## 5. ACKNOWLEDGEMENTS

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