An inverted organic solar cell employing a sol-gel derived ZnO electron selective layer and thermal evaporated MoO$_3$ hole selective layer

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We reported an efficient inverted bulk-heterojunction [regioregular of poly(3-hexylthiophene): (6,6)-phenyl C$_6$1 butyric acid methyl ester] solar cell with a highly transparent sol-gel derived ZnO film as electron selective layer and MoO$_3$ as hole selective layer. By modifying the precursor concentration of sol from 0.75 to 0.1 $M$, the optical transmittance of ZnO film increases from 75% to 95%. This improvement in transmittance increases the short-circuit density of inverted solar cell from 5.986 to 8.858 mA/cm$^2$ without sacrificing the open-circuit voltage and fill factor of the device. We also demonstrated that the device incorporated with MoO$_3$ has a larger open-circuit voltage and fill factor than the device without MoO$_3$. Power conversion efficiency of 3.09% was achieved under simulated AM 1.5G illumination of 100 mW/cm$^2$. © 2008 American Institute of Physics. [DOI: 10.1063/1.3039076]

During the past decade, organic photovoltaics (OPVs) have attracted great attention because of light weight and potentially low cost from printing at low temperature on flexible substrates. In spite of high power conversion efficiency (PCE), traditional bulk-heterojunction (BHJ) architecture has limitations in device stability due to air-sensitive low-work-function metal cathode such as Al. Diffusion of oxygen into the active layer through pinholes and gap boundaries in Al cathode causes the degradation of the active layer, leading to device instability in air. Moreover, the degradation of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):(polystyrene sulfonic acid) (PEDOT:PSS) interface is inevitable because of the strong acidic nature of PEDOT:PSS. One approach to solve this issue is using inverted structure where the charge separation and collection nature of electrode is reversed. In inverted structure, the interface of ITO/PEDOT:PSS can be avoided and low-work-function metal Al can be replaced with less air sensitive high-work-function metals such as Au and Ag. Previously, the inverted architecture with various electron-selective layers, Cs$_2$O$_3$, TiO$_x$, and ZnO (Ref. 7) were demonstrated. However, the performance of inverted cell is still lower compared to that of conventional ones. On the other hand, PEDOT:PSS is traditionally used as the hole transport layer in inverted solar cell. However, PEDOT:PSS generally needs to be fabricated in an oxygen and moisture environment (outside the glovebox) with baking, which is detrimental to the organic/polymer layer beneath. Moreover, spin casting of aqueous solution of PEDOT:PSS on hydrophobic poly(3-hexylthiophene):(6,6)-phenyl C$_6$1 butyric acid methyl ester (P3HT:PCBM) is difficult.

There are other p-type-like metal oxides, such as NiO, MoO$_3$, V$_2$O$_5$, and WO$_3$ with high work function and good hole conductivity, which have been demonstrated for hole injection in organic light-emitting diodes (OLEDs), anode buffer layer in conventional OPV, and intermediate layer in tandem organic solar cell. These oxide films can be deposited by thermal evaporation, which is compatible to thermal evaporation of anode (Au or Ag). However, there is a lack of study of inverted OPV with n-type metal oxide electron selective layer and p-type-like oxide layer. In this letter, we shall report an efficient inverted OPV employing a sol-gel derived ZnO electron selective layer and MoO$_3$ hole selective layer. We demonstrated that the PCE of inverted structure OPV is enhanced with a highly transparent sol-gel derived ZnO electron selective layer by controlling the concentration of sol. In addition, replacing commonly used PDEOT:PSS with MoO$_3$ helps to increase the fill factor (FF).

In our inverted architecture, fluorine-doped SnO$_2$ (FTO)/ZnO/P3HT:PCBM/MoO$_3$/Ag are stacked from bottom to top, as shown in Fig. 1(a). The energy level diagram of the inverted cell is depicted in Fig. 1(b). As the light enters from FTO side, the transmittance of ZnO is important in realizing high current density. The transmittance depends on the crystal size of ZnO, which in turn relies on the concentration of precursors in the sol. Therefore, we prepared sols with different concentrations of precursors using the method similar to that in literature to examine the film transmittance.

Throughout the device fabrication process, we fixed all the process parameters except the concentration of sol. Devices A, B, C, and D were fabricated from 0.75, 0.5, 0.3, and 0.1$M$ sol, respectively. We also constructed an additional device E in the same condition as device D but without MoO$_3$ layer for comparison. In our typical device fabrication process, the prepared sols were spin coated on the precleaned FTO-coated glass (15 $\Omega$/sq). The thickness of ZnO films was controlled at ~120 nm except for device A where the minimum thickness achievable was ~180 nm due to the large grain size. The synthesized films were sintered at 350 °C for 1 h in the air to obtain ZnO films. Then, a 40 mg/ml solution of P3HT:PCBM (1:1 by weight) in chloroform was cast on the ZnO film and annealed at 150 °C for 10 min in the air. Finally, Ag and MoO$_3$ were thermal evaporated from the opposite sides of substrate with a shadow mask, respectively. The thickness of Ag and MoO$_3$ was kept constant at 70 and 120 nm, respectively.
robenzene was spin cast on ZnO film to form an active layer of about 100 nm. Finally a 15 nm MoO3 and 70 nm Ag was deposited under 3 x 10^-4 Pa by thermal evaporation through a shadow mask. The fabricated devices were postannealed at 150 °C under N2 ambient for 10 min.

Photovoltaic measurement was conducted illuminating the devices under a solar simulator with AM1.5G filter. The current-voltage (I-V) characteristics were examined using a Keithley 2400 sourcemeter. The simulated light intensity was adjusted to 100 mW/cm^2 calibrated with a Thorlabs optical power meter. The I-V curves of the devices are shown in Fig. 2 and the extracted device parameters are summarized in Table I. The variation in the device performance is not significant in terms of open-circuit voltage (Voc) and FF except for device A with poor FF, which can be attributed to the recombination lost in ZnO film due to redundant thickness. However, it can be clearly seen that there is prominent changes in short-circuit current density (Jsc) compared to device A, devices B and D showed 16% and 47% improvement, respectively due to different sol concentrations. The trend in current density is consistent with variation in transmittance of ZnO films used in the devices. The optical transmittance spectra of ZnO films derived from different concentrations of sol are shown in Fig. 3(a). The average transmittance of ZnO film obtained from 0.75M is only 75%. The transmittance (device A) of more than 80% is reached beyond 700 nm, but this region does not contribute much for photon current generation because the absorption spectrum of P3HT:PCBM is negligible beyond 700 nm. Therefore, the short-circuit current density (Jsc) of device A is only 5.986 mA/cm^2. Although the transmittance of ZnO film derived from 0.3M is slightly lower than that of the film derived from 0.5M at the short wavelength region, it is higher at longer wavelength region, especially between 450 and 550 nm, where the absorption peak of P3HT:PCBM active layer is located.19 Hence, the Jsc of device is sharply increased from 6.945 to 8.086 mA/cm^2 by replacing the 0.5M sol with the 0.3M one. The optical spectrum of ZnO film derived from 0.1M sol shows not only the highest trans-

![FIG. 1.](image1.png)

**FIG. 1.** (Color online) (a) Device structure of the inverted OPV with ZnO electron selective layer and MoO3 hole selective layer and (b) the corresponding energy diagram of the inverted cell.

![FIG. 2.](image2.png)

**FIG. 2.** (Color online) The I-V characteristics of devices with ZnO films derived from different sols under simulated solar irradiation of AM 1.5G. ZnO films of devices A, B, C, and D are derived from 0.75, 0.5, 0.3, and 0.1M, respectively. Device E is the same condition as device D but without MoO3 layer.

![FIG. 3.](image3.png)

**FIG. 3.** (Color online) (a) The transmission spectra of ZnO films derived from different sols. The inset shows the relative absorption of various ZnO films near the band edge of ZnO. (b) The normalized IPCE spectra of the inverted cells.

### Table I. The summary of device performance.

<table>
<thead>
<tr>
<th>Device</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm^2)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.604</td>
<td>5.986</td>
<td>47</td>
<td>1.71</td>
</tr>
<tr>
<td>B</td>
<td>0.607</td>
<td>6.945</td>
<td>53</td>
<td>2.24</td>
</tr>
<tr>
<td>C</td>
<td>0.620</td>
<td>8.086</td>
<td>57</td>
<td>2.84</td>
</tr>
<tr>
<td>D</td>
<td>0.616</td>
<td>8.858</td>
<td>57</td>
<td>3.09</td>
</tr>
<tr>
<td>E</td>
<td>0.567</td>
<td>8.687</td>
<td>47</td>
<td>2.30</td>
</tr>
</tbody>
</table>
mittance (85%–95%) at visible range but also a lower absorbance at ultraviolet region compared with other films and hence the $J_{sc}$ of device D goes up to 8.858 mA/cm$^2$. The improvement in short-circuit current density agrees with incident photon-to-current conversion efficiency (IPCE) spectra of the fabricated devices [Fig. 3(b)]. We can see that there is no blueshift in the IPCE curves but the device with higher transparency of ZnO film has a higher photocurrent. A sharp drop in IPCE below 400 nm is clearly seen due to the strong absorption of ZnO film near the band edge of ZnO.

It is possible that the improvement in the device performance is due to better surface quality of the film, which provides better wettability and adhesion with photoactive layer.7 Therefore, surface morphology, roughness, and contact angle analysis were carried out to investigate the surface quality of ZnO films. Figure 4 shows the scanning electron microscopy (SEM) images of ZnO film deposited from different concentrations of sols. The films are composed of nanosized ZnO colloids and the grain size increases with the increase in sol concentration. The underlying mechanism of this behavior is that as the sol concentration increases, the amount of solutes increases in the sol, and thereby increasing the probability of solutes clustering together forming larger grains.7 The grain size revealed from SEM image is consistent with surface roughness measurement and larger grain size results in rougher film. The surface roughness (rms) of the films obtained from 0.75, 0.5, 0.3, and 0.1 M sol are 44.79, 18.91, 11.46, and 9.91 nm, respectively, and the water contact angle analysis were carried out to investigate the surface wettability and adhesion of the films obtained from 0.75, 0.5, 0.3, and 0.1 M sol.

In conclusion, we demonstrated the performance of inverted cell can be significantly improved by modifying the transparency ZnO electron selective layer. Inverted OPV incorporating with MoO$_3$ has higher $V_{oc}$ and FF than that without MoO$_3$ due to hole transporting and electron/exciton blocking properties. Efficiency up to 3.09% has been achieved in inverted BHJ solar cell by modifying the transmittance of sol-gel derived ZnO film to 95% and incorporating MoO$_3$.