ITO-free inverted polymer solar cells using a GZO cathode modified by ZnO

Soo-Ghang Ihn a, Kyung-Sik Shin b, Mi-Jin Jin b, Xavier Bulliard a, Sungyoung Yun a, Yeong Suk Choi a, Yungi Kim a, Jong-Hwan Park c, Myungsun Sim c, Min Kim c, Kilwon Cho c, Tae Sang Kim a, Dukhyun Choi a,1, Jae-Young Choi a, Woong Choi a,**, Sang-Woo Kim b,d,*

a Samsung Advanced Institute of Technology, Samsung Electronics, Yongin 446-712, Republic of Korea
b School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea
c Department of Chemical Engineering, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea
d SKKU Advanced Institute of Nanotechnology (SAINT) and Center for Human Interface Nanotechnology (HINT), Sungkyunkwan University, Suwon 440-746, Republic of Korea

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A B S T R A C T
A gallium-doped ZnO (GZO) layer was investigated and compared with a conventional indium-tin-oxide (ITO) layer for use as a cathode in an inverted polymer solar cell based on poly(3-hexylthiophene) (P3HT):[6,6]-phenyl-C61 butyric acid methyl ester (PCBM) bulk heterojunctions (BHJ). By modifying the GZO cathode with a ZnO thin layer, a high power conversion efficiency (3.4%) comparable to that of an inverted solar cell employing the same P3HT:PCBM BHJ photoactive layer with a conventional ITO/ZnO cathode was achieved. This result indicates that GZO is a transparent electrode material that can potentially be used to replace high-cost ITO.

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1. Introduction

Organic photovoltaic technology based on bulk heterojunction (BHJ) photoactive layers composed of conjugated polymers and fullerene derivatives has been attracting a lot of attention due to the unique applications of this technology, which are facilitated by the characteristics of the organic solar cell modules such as semitransparency, light weight, a variety of colors, and freedom of product design [1]. A simple wet-solution process and the potential for low-cost, high-throughput manufacturing based on roll-to-roll processing using low-cost, large-area flexible plastic substrates are additional advantages of this technology [2]. In BHJ polymer solar cells (PSCs), charge carriers (electrons and holes) are dissociated from photoexcited electron–hole pairs at the polymer/fullerene interfaces under illumination and are then collected at electrodes. A transparent conducting indium-tin-oxide (ITO)-coated substrate with a poly(ethylenedioxy) thiophene:poly(styrene) sulfonate (PEDOT:PSS) buffer layer is widely employed as the hole-collecting anode in PSCs, while a low work function metal, such as aluminum, with a lithium fluoride buffer layer is utilized as an electron-collecting cathode. However, the use of ITO is a barrier to low-cost manufacturing because indium is scarce and therefore expensive. Various efforts have been made to produce alternative transparent electrode materials to replace ITO in solar cells. For example, ITO-free PSCs employing classical metal grid electrodes have been studied and manufactured using roll-to-roll production; however, the performances of these ITO-free PSCs were somewhat inferior to those of PSCs containing ITO because of poor light transmission in the ITO-free PSCs [3–5]. Carbon-based nanostructured materials such as carbon nanotubes (CNTs) and graphene have also been investigated as potential alternatives to ITO. However, the sheet resistance of CNT network film is higher than that of ITO for a comparable level of transparency [6–10]. In addition, increasing the thickness of the film to reduce the sheet resistance significantly degrades its transparency. Graphene composite films also perform poorly compared to ITO films and show the same trade-off between transparency and sheet resistance [11–13].

Transparent conducting oxide (TCO) based on ZnO is one of the most important alternative transparent electrode materials because it exhibits high chemical/thermal stability, and its constituent elements are much more abundant than are those of ITO. ZnO films doped with impurities, such as aluminum (Al) [14], gallium (Ga) [15], indium (In) [16], boron [17], silicon [18],
titanium [19], and zirconium [20], exhibit not only higher conductivities but also better stabilities compared to those of undoped ZnO films. Al-, Ga-, and In-doped ZnO (AZO, GZO, and IZO) films are transparent to most of the solar spectrum used for photovoltaic solar cells, and their sheet resistances are comparable to that of ITO [14–16]. Among these materials, GZO is cheaper than IZO and more stable than AZO (more resistant to oxidation). Furthermore, the covalent bond length of Ga–O (1.92 Å) is similar to that of Zn–O (1.97 Å). Because of this small difference, only a small deformation of the ZnO lattice occurs, even at high concentrations of Ga, resulting in higher conductivity [21]. In this study, we report the fabrication and characterization of ITO-free highly efficient inverted polymer solar cells using an alternative transparent GZO cathode modified with a ZnO layer.

2. Experiment

GZO was formed using an ion-beam-assisted deposition method. Commercially available ITO-coated glass substrates were prepared, and a thin 50 nm layer of ZnO was formed on both the ITO and GZO at room temperature using the radio-frequency sputtering method. The ZnO layer was deposited in an Ar (45 sccm)/O2 (5 sccm) gas mixture at an RF input power of 200 W at room temperature using a sintered ZnO target. Then, a photoactive layer was formed from a poly(3-hexylthiophene) (P3HT):[6,6]-phenyl-C61 butyric acid methyl ester fullerene derivative (PCBM) blend with a 1:1 weight ratio in 1,2-dichlorobenzene (DCB) through spin-coating at 1000 rpm for 30 s. The sample was then dried in a covered glass petri dish [22]. Before the thermal deposition of the MoO3 buffer and the Au anode, the sample was thermally annealed at 120 °C for 5 min. The MoO3 and Au layers were of 3 and 80 nm thickness, respectively.

The optical transmittance spectra of these electrodes on glass were compared for two different wavelength ranges, and substrates are shown in Fig. 2. The integrals calculated from the optical transmittance spectra (Fig. 2) and the sheet resistance of each cathode (ITO or ZnO).

3. Results and discussion

The inverted solar cell structure employed in this study is shown in Fig. 1(a). It consisted of a glass substrate, a transparent cathode, a P3HT:PCBM BHJ photoactive layer, and a thermally-deposited MoO3/Au anode. We compared four different transparent cathodes with this device structure: ITO, ITO/ZnO, GZO, and GZO/ZnO, as shown in Fig. 1(b), (c), (d), and (e), respectively. The optical transmittance spectra of these electrodes on glass substrates are shown in Fig. 2. The integrals calculated from the spectra were compared for two different wavelength ranges, and the results of this comparison are presented in Table 1. The 500 nm GZO was chosen for use in this study because of the trade-off between sheet resistance and optical transmittance. To achieve a low sheet resistance comparable to that of ITO, a thicker GZO was needed. However, in the thicker GZO, the optical transmittance was degraded. The sheet resistances of the ITO layer and the selected 500 nm GZO were 11.9 and 24.7 Ω/sq, respectively, as shown in Table 1. The optical transmittance of the GZO layer was lower than that of the ITO layer (85.9% of ITO) for the wavelength range from 300 to 800 nm. However, considering the main absorption wavelength range of the P3HT (450–600 nm), the values are comparable (96.1% of ITO). Transmittances of ITO/ZnO and GZO/ZnO in this range were 93.3% and 93.1% of the value of ITO, respectively.

The J–V characteristic curves under illumination and the incident photon-to-current conversion efficiencies (IPCE) of the devices are shown in Figs. 3 and 4. A summary of the efficiency parameters estimated from the J–V curves under one-sun illumination (Fig. 3) and from the IPCE spectra (Fig. 4) are presented in Table 2. The shunt and series resistances (Rsh and Rs) were...
calculated from the inverse slope of the $J–V$ curves at 0 and 1.5 V, respectively [23]. There were slight differences in the short circuit currents ($J_{sc}$) but significant differences in the open circuit voltages ($V_{oc}$) and fill factors (FF) between the two groups of devices: those employing a single-layered cathode (ITO or GZO) and those employing a multi-layered cathode (ITO/ZnO or GZO/ZnO).

The devices fabricated on the single-layer transparent cathodes exhibited low $V_{oc}$ and FF values; these parameters determine power conversion efficiency (PCE). The PCE of the device with the GZO cathode was 1.85%, much lower than the reported PCE of well-developed P3HT:PCBM BHJ solar cells [22]. The inverted solar cell using a GZO cathode described by Owen et al. [15] also exhibited a low PCE (1.4%), even though that research group succeeded in improving the device performance compared to that of the normal cell structure (GZO/PEDOT:PSS/P3HT:PCBM/AI, 0.35% of PCE) by considering the work function difference between GZO and ITO. The poor performances of their cell and ours are possibly due to the substitution of GZO for ITO. However, because our inverted ITO cell also exhibited a low PCE (1.74%), we cannot simply attribute the poor performance to GZO.

The overall performances of the inverted cells improved, especially in terms of the $V_{oc}$ and FF values, when multi-layered cathodes such as GZO/ZnO and ITO/ZnO were employed. However, energy loss (in $V_{oc}$) at the cathode was significant in the devices with an ITO or GZO cathode, and the FFs of the devices using these cathodes were quite low, in accordance with the relatively low $R_{sh}$ and high $R_s$ values. These results indicate that the rectifying properties in the devices employing a ZnO layer as a cathode modifier were superior to those in the devices using only ITO or GZO. The internal built-in field formed by the work function difference between the two counter-electrodes sandwiching the BHJ photoactive layer, called symmetry breaking, is required to force transport the dissociated electrons and holes toward the cathode and anode. Despite the internal built-in field, the probability of the recombination at the electrodes resulting in a reduction in $V_{oc}$ remains high due to the unique structure of the BHJ. At the electrodes, not only can the PCBM phase form an ohmic contact, but the polymer may also form an ohmic contact with the metallic ITO or GZO [24]. Therefore, symmetry breaking through the selective transport of charged carriers within an interlayer is introduced between the BHJ photoactive layer and the electrode. Selective contact of each electrode is essential in the BHJ system to suppress recombination. Because the ZnO layer acts here as both an electron-collecting and a hole-blocking layer, recombination between the electrons collected in the ZnO layer and the holes residing in the active layer can be significantly suppressed. Performance improvement, especially in $V_{oc}$ and FF, has been achieved by incorporating hole-blocking interlayers between the active layers and cathodes [25–29].

GZO is also likely to have a symmetry breaking function because of its similar band structure to that of ZnO. GZO, however, is a highly doped degenerate semiconductor that acts more like a metal than a semiconductor, similar to ITO. In this study, we found that the ZnO layer improved the performances of devices with both ITO and GZO. To identify more clearly the reason for this performance improvement, the topology of each substrate and the morphologies of the active layers spin-coated onto the substrates were investigated because the morphology of an active layer significantly affects device performance. Fig. 5 shows 2 × 2 μm² atomic force microscopy (AFM) images of the four substrates and the active layers. The topology of ITO (Fig. 5(a)) is different from that of GZO (Fig. 5(c)). Brighter hill-like domains and darker valley-like domains with dark small dots were observable in the topography of ITO, even though these dots were not very clear. Domains were observed more clearly in the topography of ZnO on ITO (Fig. 5(b)). It appears that the ZnO thin film was not conformally deposited onto ITO. In contrast, the topography of ZnO on GZO was very similar to that of GZO.

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Efficiency (%)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>$R_{sh}$ (Ω cm²)</th>
<th>$R_s$ (Ω cm²)</th>
<th>$J_{sc}$ (cal.) (mA/cm²)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO</td>
<td>1.74</td>
<td>10.9</td>
<td>0.40</td>
<td>39.8</td>
<td>167</td>
<td>11.3</td>
<td>8.98</td>
<td>21.4</td>
</tr>
<tr>
<td>ITO/ZnO</td>
<td>3.54</td>
<td>12.05</td>
<td>0.59</td>
<td>49.8</td>
<td>269</td>
<td>3.6</td>
<td>10.35</td>
<td>16.4</td>
</tr>
<tr>
<td>GZO</td>
<td>1.85</td>
<td>10.9</td>
<td>0.41</td>
<td>41.4</td>
<td>222</td>
<td>25.5</td>
<td>9.02</td>
<td>20.8</td>
</tr>
<tr>
<td>GZO/ZnO</td>
<td>3.40</td>
<td>11.64</td>
<td>0.58</td>
<td>50.4</td>
<td>306</td>
<td>2.6</td>
<td>10.32</td>
<td>12.8</td>
</tr>
</tbody>
</table>

indicating conformal deposition of ZnO on GZO (Fig. 5d). The topology of ZnO on ITO was significantly different from that of ZnO on GZO, although the same material, ZnO, was simultaneously deposited in the same chamber under the same deposition conditions. This difference can be explained by the material compatibility between ZnO and GZO, as mentioned in the Introduction. Despite the different topologies of the substrates, there were no remarkable differences in the AFM topology images of the photoactive overlayers coated onto the substrates. Furthermore, although there was no significant difference between the topologies of GZO and ZnO or between the topologies of the active layers thereon, the respective solar cells exhibited significant performance differences. This indicates that the underlayers, namely ITO, GZO, and ZnO, did not affect the morphology of the active layer and that the morphology of the active layer was not the cause of the performance improvement; rather, symmetry breaking by the hole-blocking ZnO was responsible for the performance improvement. The counterselective layer for electron blocking and hole transporting was created with a thin MoO3 layer [30,31] in all of the devices investigated in this study.

When comparing devices using ITO/ZnO to those using GZO/ZnO, we observed only subtle differences in $R_s$ and $J_{SC}$; these devices therefore exhibited similar PCEs. The device with a GZO/ZnO cathode demonstrated a lower $R_s$ (2.6 Ω cm$^2$) than did the device with a ITO/ZnO cathode (3.6 Ω cm$^2$). We ascribed the lower $R_s$ to the better GZO/ZnO interface resulting from material compatibility between GZO and ZnO, including their similar work functions (4.4 and 4.5 eV, respectively). These similar characteristics possibly caused a lower contact resistance between the materials. The $J_{SC}$ values of the ITO/ZnO-based cell (12.05 mA/cm$^2$) and the GZO/ZnO-based cell (11.64 mA/cm$^2$) were significantly higher than the best previously reported value for P3HT:PCBM cells [13]. Considering that non-isolated universal bottom electrodes were used and that the $J$-$V$ measurements were performed without a mask, we reasoned that the measured $J_{SC}$ may have been overestimated [32]. This hypothesis was confirmed by the mismatch between the measured $J_{SC}$ and the calculated $J_{SC}$ from the EQE spectrum, as presented in Table 2. The errors were in the range of 12.8–21.4%, larger than those reported for the P3HT:PCBM cells (around 10% with 0.11 cm$^2$ of active area) [23]. We initially attributed these larger errors to the smaller active area (0.0575 cm$^2$).

It has been reported that the increased PCE of smaller cells can be explained by the reduced electrical resistive loss, the enhanced optical effects, and the finite additional fraction of photogenerated carriers in the vicinity [32,33]. In particular, we observed that cells using an ITO or GZO cathode exhibited larger errors (21.4% and 20.8%, respectively) than did cells using multi-layered cathodes. We attributed these significant errors to the higher conductivities of ITO and GZO compared to that of ZnO; this higher conductivity caused the layers to act as lateral charge carrier transport paths or additional cathodes, enlarging the effective photoactive area and volume. This result is consistent with a previous study that reported that more highly conductive PEDOT:PSS induced overestimation of the current density in a non-isolated device configuration under a flood of illumination [34]. However, despite the errors, the dependence of the measured $J_{SC}$ on the electrode type was the same as that of the calculated $J_{SC}$. Despite the relatively insignificant overestimation of $J_{SC}$, higher power conversion efficiencies were achieved from the ITO/ZnO-based inverted solar cell (3.54%) and the GZO/ZnO-based cell (3.4%) due to their higher $V_{OC}$ and FF values. These higher values were caused by the selective contact provided by the ZnO cathode-modifying layer at the cathode/polymer interface. This high performance, despite the inferior properties of our GZO layer (24.7 Ω/sq of sheet resistance and 90% average transparency in the visible spectrum) compared to those previously reported (14.3 Ω/sq of sheet resistance and 90% average transparency in the visible spectrum) [15], indicates that symmetry breaking is more important than is the quality of GZO in BHJ polymer solar cells. The PCE of our inverted-type P3HT:PCBM BHJ solar cell was quite high for a low-cost GZO cathode. To the best of our knowledge, this is one of the highest PCEs reported for inverted polymer solar cells using a ZnO cathode modifier and for polymer solar cells using a GZO electrode [35].

4. Conclusion

In summary, we synthesized and characterized an inverted P3HT:PCBM solar cell based on an alternative transparent GZO
electrode modified with a ZnO layer. Despite the relatively high sheet resistance and low optical transparency of the GZO, a high PCE (3.4%) comparable to that of an inverted solar cell based on a conventional ITO cathode (3.54%) was observed. Our results indicate that GZO is a promising low-cost transparent electrode that can be substituted for high-cost ITO, especially as a cathode in inverted-type polymer solar cells that employ a cathode modifier with appropriate material compatibility, such as ZnO.

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