Room-Temperature Indium-Free Ga:ZnO/Ag/Ga:ZnO Multilayer Electrode for Organic Solar Cell Applications

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We reported on the characteristics of an indium-free Ga-doped ZnO (GZO)/Ag/GZO multilayer electrode for use in bulk heterojunction organic solar cells. By inserting a very thin Ag layer between two GZO layers, we can fabricate a GZO-based transparent electrode with a low sheet resistance of 6 Ω/□ and a high optical transmittance of 87% at room temperature without postanneal-ling. The power conversion efficiency (2.84%) of the organic solar cell fabricated on the GZO/GZO multilayer using neutral poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is much higher than that of the organic solar cell fabricated on the GZO electrode (1.57%) annealed at 500°C. Indium-free GZO/Ag/GZO multilayer electrodes are expected to substitute for expensive indium tin oxide (ITO) electrode and decrease the cost of organic solar cells or flexible organic solar cells due to their comparable electrical and optical properties to those of crystalline ITO electrodes.

Bulk heterojunction organic solar cells (OSCs) have recently attracted considerable interest for use in the next generation of renewable energy sources due to their simple cell structure, simple process, low cost, and possibility of continuous roll-to-roll process in the atmosphere. A key merit of OSCs is their potential for low cost and large area production based on continuous roll-to-roll coating. Therefore, it is necessary to develop low cost transparent anode materials, which can be prepared at the lowest possible temperature, to enable the low cost production of OSCs. However, most OSCs reported so far are usually fabricated on transparent anodes because of their high potential for low cost and large area production based on continuous roll-to-roll coating. Consequently, a 40 nm thick top GZO layer was deposited on the thin Ag electrode at room temperature without substrate heating. After the sputtering of the bottom GZO layer, Ag layers with a high optical transmittance of 87% at room temperature without postannealing. The power conversion efficiency (2.84%) of the organic solar cell fabricated on the GZO/GZO multilayer using neutral poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is much higher than that of the organic solar cell fabricated on the GZO electrode (1.57%) annealed at 500°C. Indium-free GZO/Ag/GZO multilayer electrodes are expected to substitute for expensive indium tin oxide (ITO) electrode and decrease the cost of organic solar cells due to their comparable electrical and optical properties to those of crystalline ITO electrodes.

Table I. Comparison of electrical and optical properties of as-grown GZO (amorphous), GZO annealed at 500°C (crystalline), and GZO/Ag/GZO (amorphous) multilayer electrodes prepared at room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sheet resistance (Ω/□)</th>
<th>Resistivity (Ω cm)</th>
<th>Transmittance at 550 nm (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-grown GZO</td>
<td>1012</td>
<td>5.1 × 10^{-2}</td>
<td>78.1</td>
</tr>
<tr>
<td>GZO annealed at 500°C</td>
<td>24</td>
<td>1.4 × 10^{-3}</td>
<td>94.5</td>
</tr>
<tr>
<td>GZO/Ag (12 nm)/GZO</td>
<td>6</td>
<td>5.53 × 10^{-3}</td>
<td>87.2</td>
</tr>
</tbody>
</table>

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However, the resistivity of the GZO film that was rapidly thermal annealed at 500°C decreased by 1 order of magnitude due to the increase in the carrier concentration caused by the substitution of Ga³⁺ ions into the Zn sites in the ZnO lattice. The optical transmittance of the GZO film annealed at 500°C (94.5%) is much higher than that of the as-grown GZO film (78.1%). The optimized GZO/Ag/GZO electrode showed a very low resistivity and high transmittance even though it was prepared at room temperature without an additional annealing process. The dependence of the electrical and optical properties on the Ag thickness is shown in Fig. 1. Although the as-grown GZO electrode showed a fairly high sheet resistance and resistivity at room temperature, the insertion of the Ag layer resulted in a significant reduction in the sheet resistance and resistivity. Above a 12 nm Ag thickness, the GZO/Ag/GZO electrode shows a very low sheet resistance ($5 \times 6 \, \Omega \cdot \square$) and resistivity ($10^{-5} \, \Omega \cdot \text{cm}$), which are both much lower than those of the crystalline ITO electrode.

Figure 1. (Color online) The sheet resistance and resistivity of a GZO(40 nm)/Ag/GZO(40 nm) multilayer as a function of Ag thickness, which was continuously sputtered at room temperature.

Figure 2. (Color online) (a) Optical transmittance of GZO/Ag/GZO electrode as a function of Ag thickness. (b) Absorption wavelength region of P3HT:PCBM active layer. (c) Figure of merit value of GZO/Ag/GZO electrode calculated from sheet resistance ($R_{sh}$) and optical transmittance ($T$) at a wavelength of 550 nm as a function of Ag thickness.

Figure 3. (Color online) (a) X-ray diffraction plots of GZO annealed at 500°C, as-grown GZO, and optimized GZO/Ag (12 nm)/GZO multilayer electrode. (b) AES depth profile of optimized GZO/Ag(12 nm)/GZO electrode showing the stable interface between Ag and GZO layers.
the Auger electron spectroscopy (AES) depth profile of the optimized GZO/Ag/GZO electrode. It was shown that the individual bottom GZO, Ag, and top GZO layers were well defined without any interfacial layers due to the continuous sputtering process at room temperature. There is no evidence of an interfacial reaction between the Ag and GZO layers due to the stability of the GZO layer at room temperature. Considering the formation enthalpy of ZnO (-350.4 kJ/mol) and Ga2O3 (-1089.1 kJ/mol), the dissociation of GZO by the formation of a Ag2O (-31.1 kJ/mol) layer cannot easily occur at room temperature.53

Figure 4 shows the photocurrent density–voltage (J–V) curves obtained under 100 mW cm−2 illumination with an air mass (AM) 1.5 G condition of the OSCs fabricated on the annealed GZO and GZO/Ag/GZO electrodes. The OSCs fabricated on the GZO/Ag/GZO electrode using a conventional PEDOT:PSS layer (VP 41083) showed very poor performance with a fill factor (FF) of 0.23 and a PCE of 0.38% due to the severe reaction between GZO and conventional PEDOT:PSS. The J–V characteristics of the OSCs fabricated on the GZO electrode annealed at 500°C could not be measured due to the complete etching of the single GZO layer by PEDOT:PSS. The inset of Fig. 4a shows that the droplet of conventional PEDOT:PSS on the single GZO or GZO/Ag/GZO electrodes led to the removal of the GZO layer. Because the ZnO film was easily etched in the acidic solution, the PEDOT:PSS with pH in the range of 1–2 could remove the GZO electrode.1 Thus, we exchanged the PEDOT:PSS solution with a neutral PEDOT:PSS solution to avoid the wet etching of the GZO electrode, Figure 4b shows the J–V curve of the OSC fabricated on the annealed GZO and GZO/Ag/GZO electrodes using a neutral PEDOT:PSS solution. The OSCs fabricated on the GZO/Ag/GZO electrode grown on glass showed an open-circuit voltage (VOC) of 0.54 V, a short-circuit current (JSC) of 9.86 mA cm−2, an FF of 0.53, and a calculated PCE of ηAM1.5 = 2.84%. However, the OSC fabricated on the annealed GZO layer showed a VOC of 0.52 V, a JSC of 8.00 mA cm−2, an FF of 0.39, and a PCE of ηAM1.5 = 1.57%. Until now, there have been no reports on the fabrication of polymer solar cells with efficiency above 2% using an indium-free amorphous GZO-based electrode. Owen et al. suggested that polymer solar cells fabricated on GZO electrodes sputtered at a substrate temperature of 500°C have a very low PCE of 0.35%, which is much lower than that of the OSCs fabricated on GZO/Ag/GZO electrodes.7 By further optimization of the PEDOT:PSS coating conditions and surface treatment of the GZO electrode, the performance of the OSCs fabricated on the GZO/Ag/GZO multilayer electrode might be improved. Although the GZO/Ag/GZO multilayer electrode possesses expensive Ga and Ag elements, the GZO/Ag/GZO multilayer electrode could be expected to be a low cost and indium-free TCO electrode substitute for the conventional ITO electrode because the amount of Ga (3 wt % Ga2O3-doped ZnO) and Ag (~12 nm) elements in the GZO/Ag/GZO multilayer is fairly small.

In summary, we propose an indium-free and low cost GZO/Ag/ GZO multilayer electrode grown by dual-target sputtering at room temperature as a viable alternative to ITO electrodes for the low cost production of OSCs or flexible OSCs. By making use of the low resistivity and antireflection effect of the inserted 12 nm thick Ag layer, we obtained a GZO/Ag/GZO electrode with a very low sheet resistance of 6 Ω/□ and a high transmittance of 87%, although all of the layers were fabricated at room temperature, unlike those in a crystalline ITO electrode. The J–V performance of the OSCs fabricated on the indium-free GZO/Ag/GZO electrode indicates that the GZO/Ag/GZO electrode is a promising low cost and room-temperature-processed TCO electrode that can be used as a substitute for the high cost ITO electrode in OSCs and flexible OSCs.

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References


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