The annealing effects of tungsten oxide interlayer based on organic photovoltaic cells

Sang Bin Lee, Jin Ho Beak, Byung hyun Kang, Ki-Young Dong, Youn-Yeol Yu, Yang Doo Lee, Byongsung Kwon

Abstract
We investigated the effect of tungsten oxide (WO$_3$) interlayer as a hole collection layer on the performance of organic photovoltaic cells according to the thickness and temperature of the interlayer. The characteristics of organic photovoltaic cells such as fill factor, current density, and open circuit voltage are continuously improved by increasing the temperature of the WO$_3$ interlayer. The surface of a treated WO$_3$ film promotes the crystallization of P3HT because an annealed WO$_3$ film is more hydrophobic than a pristine WO$_3$ film.

Highlights
• The performance of organic photovoltaic cells is improved by increasing the temperature of the WO$_3$ interlayer.
• The surface of an annealed WO$_3$ film promotes the crystallization of P3HT because an annealed WO$_3$ film is more hydrophobic than a pristine WO$_3$ film.
• The work function of the WO$_3$ film after annealing increases until a hole can be smoothly transferred.
• The device fabricated with a WO$_3$ film of 40 nm thickness and at 350 °C showed the highest FF and PCE of OPVs.
The annealing effects of tungsten oxide interlayer based on organic photovoltaic cells

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A R T I C L E   I N F O

Article history:
Received 18 February 2013
Received in revised form 23 April 2013
Accepted 9 May 2013
Available online 26 June 2013

Keywords:
Tungsten oxide
Thermal annealing
Organic solar cell
Organic photovoltaic cell

A B S T R A C T

We investigated the effect of tungsten oxide (WO3) interlayer as a hole collection layer on the performance of organic photovoltaic cells according to the thickness and temperature of the interlayer. The characteristics of organic photovoltaic cells such as fill factor, current density, and open circuit voltage are continuously improved by increasing the temperature of the WO3 interlayer. The surface of a treated WO3 film promotes the crystallization of P3HT because a treated WO3 film is more hydrophobic than a pristine WO3 film. Furthermore, the energy barrier between P3HT and the WO3 interlayer is minimized since the work function of the WO3 film after annealing progressively increases until a hole can be smoothly transferred. Therefore, organic photovoltaic cells using an interlayer of treated WO3 film have higher hole mobility and better efficiency. The efficiency of an organic photovoltaic cell with a 40 nm-thick WO3 interlayer is significantly enhanced from 0.94 to 3.04% as the temperature changes from room temperature to 350 °C under AM 1.5G illumination.

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1. Introduction

Organic photovoltaic cells (OPVs) have been studied as a type of next generation energy source because they are lightweight and flexible, showing much potential for large scale fabrication through a low-cost process [1]. During the past 30 years since the development of OPVs, OPVs technologies have focused on increasing power conversion efficiency (PCE), lifetime and reliability. Many methods have been proposed to improve the performance of OPVs, such as the use of a bulk heterojunction structure [2], the use of an optical spacer over the active layer using titanium oxide (TiO2) [3], annealing to improve the crystallization of poly-3 (hexylthiophene) (P3HT) polymer [4], and O2-plasma treatment on indium tin oxide (ITO) for work function modification [5].

Also, thin interlayers between the active layer and the electrodes were introduced to extract diffused holes or electrons, easily. A polymer complex of poly(3,4-ethylenedioxythiophene) and poly (styrene sulfonate) (PEDOT:PSS) has been preferred for OPVs [6,7] because it has flexibility, high transparency and good hole mobility on an ITO layer. Furthermore, it has a high work function, which can be used to match the band structure between the donor layer and the anode. However, the PEDOT:PSS interlayer has several disadvantages that reduce the performance of OPVs, such as stability and life-time due to the fact that PSS, which is highly acidic, corrodes the ITO layer chemically and that PEDOT:PSS degrades under UV illumination [8–11]. For solving these problems, several proposals such as alternative materials of PEDOT: PSS, ITO-free devices [1,12,13], and inverted architecture device [14] have been studied.

Recently, as replacement for PEDOT:PSS, metal oxides have been used to form attractive hole extracting layers because they do not have side effects such as degradation and chemical reaction with ITO. Nickel oxide (NiO) [15], vanadium oxide (V2O5), molybdenum oxide (MoO3) [16] have been researched as materials for the interlayer, such as the hole-selective or electron-selectivity layer. Especially, tungsten oxide (WO3) has been investigated as an effective hole collection layer because it has a high work function, high ionization potential (IP) and p-type electronic property [17]. Also, the surface morphology of a WO3 layer is much smoother than those of MoO3 and V2O5 layers. It can also reduce the leakage current because the bias-dependent carrier recombination is prevented because the local high electric fields were not formed at a smoothened surface of an interlayer or electrode [18]. The WO3 interlayer deposited by thermal evaporation as an anodic interlayer was reported to have increased the performance of OPVs [19]. In inverted OPVs, the WO3 layer between the active layer and the top electrode improved the efficiency of the OPVs from 0.13 to 2.58% [20].

In this work, OPVs are fabricated with WO3 interlayers, instead of the PEDOT:PSS layer, between the active layer and the anode to collect holes. We investigated the effect of WO3 layers of various
thickness and annealing temperatures which changes from room temperature to 350 °C on the performance of organic photovoltaic cells. We discussed the function of an annealed WO3 interlayer, which significantly improved the performance of an OPVs device. The physical, optical and electronic properties of a thermal evaporated WO3 thin film are measured by AFM, IPCE, XPS and XRD.

2. Experimental

Fig. 1 shows the structures of OPVs with WO3 interlayers of different thicknesses and temperatures. The patterned ITO substrates of 25 Ω/square were ultra-sonically cleaned several times in acetone, methanol and de-ionized water sequentially. The cleaned substrates underwent UV-Ozone treatment for 15 min and treated with oxygen plasma at 90 W for 240 s. A WO3 (purchased from KOJNDO KOREA, 99.99%) thin film was deposition onto an ITO substrate by thermal evaporation in vacuum of about 1 × 10⁻⁶ Torr at evaporation rate of 4.0 Å/s. The thicknesses of the WO3 films were detected in situ by a quartz monitor.

The deposited WO3 thin films were annealed in Ar atmosphere in a glove box at different temperatures (room temperature (RT), 200 °C, and 350 °C) for 30 min using a hot plate. The ITO glass substrate below WO3 was kept in the glove box of Ar environment for 10 h after thermal annealing to cool down.

In order to fabricate bulk hetero-junction organic solar cells, P3HT (purchased from Rieke metals, Inc.) and PCBM (purchased from Nano-C, Inc.) were dissolved in mono-chlorobenzene (CB, 40 mg/ml) for 14 h and blended at a mixing ratio of 1:0.6 for 2 h in a glove box (Ar atmosphere). The blended active mixture was spin coated at 900 rpm for 30 s to form a film, which was then thermally annealed at 140 °C for 15 min in Ar atmosphere. The Al cathode (100 nm) and the interlayer (LiF 0.6 nm) were thermally evaporated in vacuum greater than 5 × 10⁻⁷ Torr.

The current-voltage (I-V) characteristics of the fabricated devices were subjected to simulated AM 1.5 global solar irradiation of 100 mW/cm² incident power density using a 300 W Xe lamp (Mc science) and measured using a Keithley 2400 source meter. Moreover, Incident-Photon-to-electron Conversion Efficiency

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 nm</td>
<td>6.94</td>
<td>0.53</td>
<td>31</td>
<td>1.15</td>
</tr>
<tr>
<td>10 nm</td>
<td>7.10</td>
<td>0.53</td>
<td>35</td>
<td>1.33</td>
</tr>
<tr>
<td>20 nm</td>
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<td>0.52</td>
<td>36</td>
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<td>0.55</td>
<td>44</td>
<td>1.90</td>
</tr>
<tr>
<td>40 nm</td>
<td>7.79</td>
<td>0.60</td>
<td>64</td>
<td>3.04</td>
</tr>
<tr>
<td>50 nm</td>
<td>7.46</td>
<td>0.58</td>
<td>46</td>
<td>2.00</td>
</tr>
<tr>
<td>60 nm</td>
<td>6.91</td>
<td>0.51</td>
<td>32</td>
<td>1.15</td>
</tr>
</tbody>
</table>

Fig. 1. Structure of OPVs with WO3 interlayer of different thicknesses for different temperatures: ITO/WO3/P3HT:PCBM/LiF/Al.

Fig. 2. J-V characteristics under 100 mW/cm² white light illumination in air for devices with WO3 interlayers of different thicknesses between the active layer and ITO.

Fig. 3. (a) The J-V characteristics under 100 mW/cm² white light illumination in air for devices according to different temperature. (b) The Incident-Photon-to-electron Conversion Efficiency (IPCE) according to different temperatures.
(IPCE) was measured as a function of wavelength from 300 to 800 nm (PV Measurement).

After the WO3 thin film was thermally evaporated on ITO, its surface morphology and grain size were measured by atomic force microscopy (XE-100, Park systems Inc). X-ray photoelectron spectroscopy (XPS) measurements were performed with monochromatized Al Kα X-ray photons (hv=1486.6 eV for XPS) (K-Alpha, Thermo Electron, Inc.). The contact angle was measured in atmospheric air at room temperature using a commercial contact angle meter. X-ray diffraction (XRD) measurements were obtained by an X-ray diffractometer (Xpert APD, PHILIPS). The work function of a WO3 film under a UV source was measured by a photoelectron spectrometer (AC-2, Riken Keiki Inc.) at atmospheric pressure.

3. Result and discussion

The optimal thickness of the WO3 layer for increasing the performance of OPVs has been reported previously [19–21]. But, the properties of the WO3 layer differ according to how to prepare material or equipment and process. For this reason, we investigated several thicknesses in the range between 5 nm and 60 nm at the same temperature to find the adequate efficiency of OPVs. Fig. 2 and Table 1 show the performances of OPVs for different thicknesses of the WO3 layer under 100 mW/cm² white light illumination. The performance of OPVs improved with increasing WO3 thickness up to 40 nm. The efficiency of OPVs, however, decreased with the thickness of WO3 layer over 40 nm. A WO3 layer of 40 nm thickness was found to be the optimal thickness for yielding the best performance of OPVs.

Fig. 3(a) and Table 2 show the characteristics of the OPVs according to temperature with a 40 nm-thick WO3 layer. We focused on the thermal annealing effect because it significantly increased OPVs performance, as described. But the processing temperature was limited to 350 °C because the crystalline nature of WO3 would be changed at temperatures over 400 °C. The device with the pristine WO3 layer exhibited power conversion efficiency (PCE) of 0.94% at a very low fill factor (FF) of 29.9%. The short-current density (Jsc) and open voltage (Voc) are 6.00 mA/cm² and 0.52 V, respectively. However, the device with the annealed WO3 layer showed improved PCE of 3.04% at FF = 64.47%, Jsc = 7.79 mA/cm² and Voc = 0.60 V. The improved performance characteristics of OPVs, such as FF, Jsc, and PCE, are closely related to the decrease of the series resistance (Rₛ) of devices [22]. We demonstrated an IPCE spectrum of the fabricated devices in Fig. 3(b). The IPCE is defined as the ratio of photogenerated charge carrier per incident photon. As shown, IPCE improved for every wavelength by the thermal annealing process. The thermal treated device at 350 °C had a maximum IPCE of 71% at 444 nm; on the other hand, the

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Jsc 100</th>
<th>Voc 100</th>
<th>FF 100</th>
<th>PCE 100</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
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<td>0.52</td>
<td>29.9</td>
<td>0.94</td>
</tr>
<tr>
<td>200</td>
<td>7.58</td>
<td>0.59</td>
<td>48.9</td>
<td>2.20</td>
</tr>
<tr>
<td>350</td>
<td>7.79</td>
<td>0.60</td>
<td>64.47</td>
<td>3.04</td>
</tr>
</tbody>
</table>

Table 2: Short-circuit current density (Jsc), open-circuit voltage (Voc), FF, and power conversion efficiency (PCE) of OPVs according to the annealing temperature.

Fig. 4. AFM images (a) bare-ITO, (b) WO3 on ITO (RT), (c) WO3 on ITO (200 °C) and (d) WO3 on ITO (350 °C).
pristine device had a maximum IPCE of 57% at the same wavelength. Since the absorption spectra of P3HT exist near visible spectrum of about 300–700 nm and the maximum peak is about 450 nm [23], this enhanced IPCE (annealed WO3 film than pristine WO3 film) at 444 nm region is supposed to be oriented form characteristic of P3HT layer using annealed WO3 interlayer. To analyze these phenomena, surface analysis was performed by AFM, XPS, XRD.

We measured the surface morphology of the WO3 layer by Atomic Force Microscopy (AFM) to investigate the effect of annealing after it was evaporated from the ITO. AFM images of the surface morphologies of the bare-ITO and WO3 film annealed at different temperatures (RT, 200 °C and 350 °C) are shown in Fig. 4. As shown in Fig. 4(b), the surface morphology of the WO3 film deposited on the ITO without the annealing process is smoother than that of the bare-ITO at Fig. 4(a), as reported by other researchers about WO3 films [24,25]. Also, the surface morphology of the WO3 film with increasing temperature in Fig. 4(c) and (d) is more rough than that of the pristine WO3 film. Nevertheless, WO3 films annealed at 350 °C still have smooth surface, amorphous state and nanosized grains because treated temperature is low for changing the nature of WO3 crystallization [24]. The Root Mean Square (RMS, Rq) values of roughness were 3.94 nm, 1.46 nm, 1.55 nm and 1.71 nm. Therefore, the WO3 interlayer has a smoother morphology than the bare-ITO. This smoother morphology could be the reason for the increased performance of OPVs because it is known to be very effective in decreasing dark current and contact resistance [26].

Chemical characterization of the WO3 film with increasing temperature was carried out by XPS. Fig. 5 shows the W4f peak and the O1s peak of the WO3 films at different temperatures, which were obtained by XPS analysis. The W4f peak did not remarkably change the state of the tungsten compounds according to increasing temperature. O1s peak was deconvoluted into three components such as oxygen atoms (O2−), which are involved in the formations of strong W=O bonds at binding energy of about 531 eV, hydroxyl group (OH−) at about 532.5 eV and water molecule (H2O), which are absorbed at the surface of WO3 film at about 533.5 eV [27]. The pristine WO3 film had a compound of water molecules at about 533.5 eV in Fig. 5(a). However, the H2O peaks disappeared after the annealing process at over 200 °C because the trapped water molecules on the surface of the WO3 film were diffused by thermal energy, as shown in Fig. 5(b) and (c). Also, oxygen atoms (O2−) peak moved to lower energies with increasing annealing temperature. These changes mean that amount of the state of W=O bonding in the WO3 film was increased [28]. Therefore, a heat treated WO3 film has a more hydrophobic surface than a pristine WO3 film.

The wetting property of the interlayer under an active layer can affect the growth of P3HT films. The contact angles of a WO3 film according to different temperatures are described in Fig. 6 inset. The contact angle measurements were performed using a 2 μl DI-water. A droplet was injected on the surface of the thermally evaporated WO3 films after the annealing process. WO3 surface after annealing process is more hydrophobic than the pristine WO3 surface. According to previous studies, hydrophobic surfaces or self-assembled monolayer (SAM) treatment promotes the crystallization of P3HT films [29,30]. Furthermore, Li Destri et al. reported that a hydrophobic surface greatly prevents the aggregation of PCBM and highly in-plane oriented P3HT lamellae [31]. As shown in Fig. 6, the P3HT films that were grown on the thermal treated WO3 films demonstrated higher degree of ordering than those that were grown on the pristine WO3 films. The higher crystallization of P3HT on the annealing WO3 film is expected to improve the hole mobility of P3HT films.

Fig. 5. XPS: variations of the W(4f) peak and the O(1s) peak for different thermal annealing processes.
To study the effect of increased P3HT crystallization on hole mobility by using an annealed WO$_3$ film, which has a more hydrophobic surface than a pristine WO$_3$ film, we measured hole mobilities using hole-only devices having the structure of ITO/WO$_3$ (40 nm)/P3HT (140 nm)/Au with different WO$_3$ films. Fig. 7 shows the current density ($J$)–voltage ($V$) characteristics of the hole-only devices as log–log plots. The treated WO$_3$ film based devices exhibited a better device-to-device reproducibility than the pristine WO$_3$ film based devices. Also, each hole mobility was calculated by the following space-charge-limited current (SCLC) equation [32]:

$$J = \frac{9e_0 \varepsilon_r \mu V^2}{8L}$$

where $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_r$ is the relative dielectric constant (value of P3HT is 3.4 [33]), $\mu$ is the carrier mobility, and $L$ is the P3HT film thickness. The mobility of each hole extracted from this equation was $2.0 \times 10^{-4}$ cm$^2$/V s for the pristine WO$_3$ film based device, $2.4 \times 10^{-4}$ cm$^2$/V s for the 200 °C annealed device and $3.6 \times 10^{-4}$ cm$^2$/V s, for the 350 °C annealed device. The efficiency of the OPVs based, annealed WO$_3$ films was improved by the increased carrier mobility, which decreased the possibility of space-charge build-up [34] or reduced bias-dependent recombination [35].

We studied the work function of the WO$_3$ film with increasing annealing temperature to determine its effect on the energy decrease of the device between the interlayer and the active layer. Fig. 8 shows the work function variations of the WO$_3$ film treated by thermal treatment. The work function of the WO$_3$ film increased with increasing temperature. The obtained work functions were 5.03 eV, 5.12 eV and 5.17 eV for the pristine WO$_3$ film, for the WO$_3$ film annealed at 200 °C and for the WO$_3$ film annealed at 350 °C, respectively. Generally, the hole collection at the interface of the anode and active layer increased when the work function of the interlayer well matched the work function of the donor type material such as P3HT [36]. As the work function of the annealed WO$_3$ film gradually approached the energy level of the HOMO of P3HT (5.2 eV), the energy barrier between P3HT and WO$_3$ film was minimized. Thus, the hole which was created in the active layer easily transferred from the active layer to the anode. Also, a higher work function of the treated WO$_3$ film improved the apparent hole mobility and then increased the hole mobility induced by FF [37]. Therefore, the treated WO$_3$ film can be expected to be an efficient hole collection interlayer material.

4. Conclusion

We demonstrated tungsten oxide as an interlayer between ITO and P3HT:PCBM for different thicknesses and temperatures for BHJ structure organic photovoltaic cells. The device fabricated with a WO$_3$ film of 40 nm thickness and 350 °C showed the highest FF and PCE of OPVs. Increased performance of OPVs was studied by measuring the characteristics of WO$_3$ films and devices that were annealed. The morphology of the treated WO$_3$ film was not significantly changed, but its surface became more hydrophobic to improve P3HT crystallization and increase hole mobility of the device. Furthermore, the increased work-function of the treated WO$_3$ film improved hole-collection efficiency because it reduced the barrier between P3HT and ITO. The heat treated WO$_3$ film may be used as an efficient hole collection material for OPVs.

Acknowledgment

This work was supported by the RFID R&D program of MKE/KEIT. (10035225, Development of core technology for high performance AMOLED on plastic).