Effects of Sn Incorporation in ZnO Thin Films on Properties of Perovskite Solar Cells

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Abstract. Properties of electron transporting layer (ETL) play an important role on photovoltaic performances of perovskite solar cells. In this work, effects of Sn incorporation on properties of ZnO-based perovskite solar cells were investigated. Sn-doped ZnO (TZO) thin film as ETL was prepared via a sol–gel method. With 5% atom doping, TZO film coated on an indium doped tin oxide (ITO) substrate provided comparable light transmittance with that of an undoped ZnO/ITO substrate. It was also found that the optical band gap of TZO film (3.30 eV) is slightly wider than that of the ZnO one (3.28 eV). These results suggest that Sn atoms probably incorporated into the ZnO crystal during the sol-gel method. The grains size of perovskite layer coated on TZO or ZnO films also showed variation. The perovskite crystal on the TZO thin film (average 300 nm) was larger than that of the one on ZnO thin film (average 277 nm). The preliminary results indicate that the perovskite solar cell based on TZO film provided higher power conversion efficiency (PCE) of 4.42 % than the ZnO-based device (3.16%). Short-circuit current density ($J_{sc}$), open-circuit voltage ($V_{oc}$) and fill factor (FF) of TZO-based device were also higher than the ZnO-based device. This may be because TZO film may provide lower resistivity and better ETL/perovskite interface contact, confirmed by lower series resistance and higher shunt resistance of the TZO-based device. Finally, this work introduced a simple method to prepare TZO film at low temperature for photovoltaic application. It may help guide the development of flexible solar cells and other optoelectronic devices.

1. Introduction
Solar energy is a very important energy source because it is renewable, inexpensive, and clean [1]. Perovskite solar cell (PSC) is an emerging type of solar cells and it is very promising for future light-to-electricity conversion. Since the past few years, the PSCs have been developed rapidly because of their excellent semiconducting properties; tunable band gap [2], simple deposition process, low-cost[3], wide-range light absorption, long carrier diffusion length, and high carrier mobility [3].

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PSCs can be constructed by sandwiching a perovskite layer with electron transporting layer (ETL) and hole transporting layer (HTL). Zinc oxide (ZnO) is one of the materials using as ETL [4] because it provides good properties of n-type semiconductor such as wide-direct band-gap energy (3.37 eV), high exciton binding energy, non-toxicity, high transparency, and applicability for flexible devices [4-5].

In order to prepare flexible substrates, the ZnO ETL is required to be processed at low temperature due to low heat resistance of plastic substrate [5]. However, the electron mobility of ZnO film prepared at low temperature is relatively low in comparison to the film processed at higher temperature [4]. This film may result in poor device performance [4]. Therefore, ZnO should be modified by introducing element dopants to enhance its electrical properties [7-9].

In this work, Sn atoms were incorporated into the ZnO thin films via a sol-gel method. The molar ratio of Sn/(Zn + Sn) was fixed at 5% since this ratio provided the optimum improvement in film conductivity.[10] The optical properties of Sn-doped ZnO (TZO) thin film were also investigated. The improvement in photovoltaic performances was achieved with TZO film was used as ETL.

2. Experimental

2.1 Preparation of TZO thin films
An indium tin oxide (ITO) glass substrate was patterned using Zn powder and 1 M of HCl solution. Then, the substrate was sonicated in 1% w/v Alconox solution, deionized water (DI), acetone and isopropanol for 30 min each. The cleaned ITO glass substrate was treated with UV-ozone cleaner for 30 min. A TZO precursor solution was prepared by dissolving Zn(CH$_3$COO)$_2$·2H$_2$O and SnCl$_2$·2H$_2$O in 2-methoxyethanol with a total metal concentration of 0.50 mol/L. The mixture was stirred overnight at room temperature. The molar ratio of Sn/(Zn + Sn) was fixed at 5% [9]. Compact TZO layers were deposited onto the cleaned ITO substrates by spin-coating the precursor solution on the cleaned ITO substrate at 3,000 rpm for 60 s. The substrate was then annealed on a hot plate at 160 °C for 1 h.

2.2 Preparation of device
A PCBM layer was coated on the TZO layer by spin-coating a PCBM solution in chlorobenzene at 2000 rpm for 30 s. The films were annealed at 70 °C for 5 min. A perovskite layer was prepared via two-step sequential deposition [11]. A 1 M of PbI$_2$ solution in N,N-Dimethyl formamide (DMF) with 120 µl of 4-tert-butylpyridine (tBP) was deposited on the TZO substrate by spin-coating at 3,000 rpm for 30 s and annealing on a hotplate at 100 °C for 60 min. After cooling to room temperature, a mixture of FAI (HN=CHNH$_2$H) and MAI (CH$_3$NH$_3$I) with molar ratio of 4:6 in isopropanol was dropped on the PbI$_2$ layer in a N$_2$-filled glove box at relative humidity of less than 20%. Then, it was spin-coated at 2,000 rpm for 30 s. The as-deposited film was annealed on a hotplate at 75 °C for 20 min to form MA$_{0.83}$FA$_{0.17}$PbI$_3$. A dopant-free poly (3-hexylthiophene-2,5-diyl) or P3HT layer was formed by spin-coating a 20 mg/ml P3HT solution in chlorobenzene at 1,000 rpm for 30 s. Finally, Au metal electrode was deposited by thermal evaporation on the P3HT layer.

2.3 Characterizations
UV–vis spectroscopy (Lambda35 spectrophotometer) was used to investigate optical properties. The average transmittance was defined as an arithmetic mean of the transmittance values over 300-800 nm [12]. Field emission scanning electron microscope (FE-SEM) was carried out to observe and characterize perovskite morphology. The FE-SEM images were analyzed by randomly measuring the sizes of 130 grains using ImageJ software in order to determine grain size distribution. Photocurrent-voltage measurement under solar light AM 1.5 at 1,000 mW/cm$^2$ was carried out to characterize photovoltaic properties of perovskite solar cells. A photomask with area of 0.038 cm$^2$ was used to define irradiated active area.
3. Results and Discussion

To investigate the effects of Sn incorporation on optical properties, transmittance and absorbance of TZO films were measured. The transmission spectra of ZnO and TZO thin films on ITO substrates were shown in figure 1a while the absorption spectra were shown in figure 1b. It is found that the average transmittances are 78.47 % for ZnO film and 77.94 % for TZO one. The absorbance of the TZO film is significantly lower than that of the ZnO film. These results may be affected by the Sn incorporation.

In addition, the energy gap ($E_g$) of these films was calculated in order to roughly confirm the presence of Sn atoms in the ZnO film. The optical bandgap of the films was determined by plotting $(\alpha h \nu)^{2}$ as a function of the photon energy ($h \nu$), as shown in figure 1c. Note that $\alpha$, $h$, and $\nu$ are absorption coefficient, Plank’s constant and photon frequency, respectively.

The $E_g$ values of these films were determined by the following equation;

$$(\alpha h \nu) = \beta (h \nu - E_g)^m$$

where $m$ is constant which depends on types of optical transition. In this case, since ZnO is direct band gap material, $m$ is 1/2. The extrapolation of this linear line intercepted the x-axis gave the $E_g$ value. The $E_g$ of ZnO film and TZO films were approximately 3.28 and 3.30 eV, respectively. The change in $E_g$ values could be influenced by the Sn incorporation.

The perovskite layers were deposited on ZnO and TZO films by two step deposition technique. FE-SEM images of perovskite films on those samples were showed in Figure 2. The average grain size of perovskite materials on TZO film is approximately 302 nm and that on ZnO film is approximately 277 nm.

To further verify the Sn-doping effects on photovoltaic performances of perovskite solar cells, photocurrent-voltage ($I-V$) measurement was performed. The photovoltaic parameters were evaluated and summarized in Table 1. The perovskite solar cell based on TZO film provided an average power conversion efficiency (PCE) of 4.19 % (maximum PCE of 4.42%). These values are higher than that of the device based on ZnO film (average PCE of 3.11% and maximum PCE of 3.16%). It was also found...
that short-circuit current density ($J_{sc}$), open-circuit voltage ($V_{oc}$) and fill factor (FF) of the TZO device are higher than those of the ZnO device. The reason behind this improvement can be attributed to higher shunt resistance ($R_{sh}$) and lower series resistance ($R_s$) of the TZO device over the ZnO one. These results imply that the contact resistances between the active layer and electrodes was improved and charge transport may be facilitated due to the Sn incorporation.

Table 1. The average photovoltaic parameters of perovskite solar cells fabricated in this work. The maximum PCE is shown in the parentheses.

| ETM  | $V_{oc}$ (V) | $J_{sc}$ (mA cm$^{-2}$) | FF  | PCE (%)  | $R_{sh}$ (Ωcm$^2$) | $R_s$ (Ωcm$^2$) |
|------|-------------|-------------------------|-----|----------|---------------------|----------------|
| TZO  | 0.94        | 9.20                    | 0.48| 4.19(4.42)| 78                  | 16             |
| ZnO  | 0.87        | 8.59                    | 0.42| 3.11(3.16)| 340                 | 28             |

4. Conclusions
Sn atoms could be incorporated into ZnO thin film, forming TZO film. The perovskite solar cell based on TZO film provide the enhanced photovoltaic performances. This improvement is due to better interfacial property and charge transport. Finally, this work introduced a simple method to prepare TZO film at low temperature for photovoltaic application. It may help guide the development of flexible solar cells and other optoelectronic devices.

5. References
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