The Effect of Transparent Conductive Oxide Substrate on the Efficiency of SnGe-perovskite Solar Cells

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The efficiency of Sn-perovskite solar cells has been dramatically improved by adopting the inverted structure solar cells and is expected to reach the efficiency of lead-based perovskite solar cell. We have observed fluctuations in the efficiency of the same perovskite material due to the type of TCO substrates. In this study, we investigated the influence of TCO substrates on the solar cell characteristics of SnGe-perovskite solar cells. It was found that the efficiency of the SnGe-perovskite solar cell is better with fluorine-doped tin oxide (FTO) substrate (9.24%) than indium-doped tin oxide (ITO) substrate (7.72%). The improvement of the efficiency of the cell with FTO substrate is contributed by the improvement in the short-circuit current $J_{sc}$ and $V_{oc}$. The high transmittance of FTO substrate enhanced the $J_{sc}$ while the $V_{oc}$ is influenced by the Fermi level of the transparent conductive oxide film. Although there is a difference in the surface roughness between TCO substrates, there is no direct influence on the device performance that can be observed.

Keywords: Perovskite solar cells, Inverted structure, Pb free, Transparent conductive film, Fluorine-doped tin oxide, Indium-doped tin oxide

1. Introduction

Perovskite solar cells hold promise as the next-generation solar cells due to the high-power conversion efficiency despite simple solution-processed spin-coating technique. As a result of accelerated research in this field, the power conversion efficiency has reached 23.7% in a device with 0.01 cm$^2$ (20.5% for 1 cm$^2$ area) and is growing close to that of polycrystalline Si and other compound solar cells [1,2]. A perovskite solar cell utilizes a perovskite compound as the light absorber having the chemical structure of $ABX_3$. Perovskite is composed of organic and inorganic components where A is the monovalent cation, B is the divalent metal and X is halide ion. The first perovskite compound reported was CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) which is a lead-based perovskite material [3], which is the mainstream of the perovskite material showing the highest power conversion efficiency to date [4-10]. However, due to the toxicity of lead, the use of lead in electronics is prohibited by the RoHS regulation. Because of this, the social expectation of lead-free perovskite solar cells is very high [11]. As an alternative candidate to lead-based perovskite, tin-based perovskite has been gaining attention of the scientific community. Compared to other lead-free perovskites which has efficiency less than 5% [12-17], tin-based perovskite solar cell shows the most promise with the highest power conversion efficiency reported so far reaching 9.6% [18].

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most report, tin-based perovskite solar cells adopt inverted structure solar cells allowing more flexibility in terms of the types of charge transporting material that can be used as high processing temperature is not needed in this case. Hence, the selectivity of the transparent conductive film (TCO) glass is enhanced for the same reason. At present, typically ITO substrate is used for inverted type solar cells [19-22]. ITO substrates are superior to FTO substrates in terms of sheet resistance [23,24]. However, the cost of ITO substrates is more expensive than FTO substrates. Furthermore, there is a report suggesting that FTO substrate gives higher performance than devices prepared on ITO substrate [25]. However, the cause of this higher efficiency is not described in detail. Moreover, not only the type of TCO but also the surface shape may affect the conversion efficiency. Therefore, this report compares the power conversion efficiency of SnGe-perovskite solar cells using 3 different TCO substrates namely, Flat-ITO, Flat FTO, and FTO with texture. The highest performance was obtained with FTO with texture substrate followed by Flat FTO substrate and then Flat-ITO.

2. Experimental

2.1. Material

Tin (II) iodide (SnI₂, 99.99 %, Sigma Aldrich), tin (II) fluoride (SnF₂, 99 %, Sigma Aldrich), Germanium (II) iodide (GeI₂, 99.9 %, Sigma Aldrich), Formamidinium iodide (FAI, >98.0 %, TCI), N,N-Dimethylformamide (DMF, 99.8 %, Sigma Aldrich), Dimethyl sulfoxide (DMSO, ≥99.9 %, Sigma Aldrich), and other solvent employed in this report were used without further purification. EDAI is synthesized using the procedure as reported by Zhang et al. [26].

Flat ITO, Flat FTO, and FTO with texture glass were purchased from GEOMATEC CO. Ltd., SPD laboratory, Inc., AGC Inc., respectively. These TCO layers were fabricated by sputter deposition, spray pyrolysis deposition and chemical vapor deposition, respectively.

2.2. Preparation of perovskite film

5 mol% GeI₂-doped FA0.98EDA0.02SnI₃ solution (0.9 M) is prepared by dissolving SnI₂ (335.3 mg), SnF₂ (14.1 mg), FAI (151.7 mg), EDAI (2.8 mg), and GeI₂ (14.7 mg) in DMF (800 µL) and DMSO (200 µL). These solutions are prepared in a nitrogen-purged glovebox.

2.3. Device fabrication

The TCO glass substrates are cleaned with detergent, deionized water, acetone and isopropyl alcohol in an ultrasonic bath for 15 min., respectively. The cleaned TCO substrates are then treated with oxygen plasma for 5 min. PEDOT:PSS filtered with 0.45 µm PVDF filter is spin-coated on the cleaned TCO substrates at 500 r.p.m for 9 s, and 5000 r.p.m for 50 s. After that, the substrates are annealed at 140 °C for 20 min. The perovskite precursor solution is then spin-coated on the TCO substrates at 5000 r.p.m for 50 s with chlorobenzene used as the anti-solvent. All perovskite films are annealed on a hotplate at 70 °C for 10 min. Subsequently, C₆₀ (thickness of 25 nm), BCP (7 nm), Ag (80 nm), Au (20 nm) are sequentially evaporated by thermal evaporation under vacuum, resulting in an active area of 0.405 cm².

2.4. Characterizations

The XRD patterns were obtained by a Rigaku Smartlab X-ray diffractometer with monochromatic Cu-Kβ irradiation (45 kV / 200 mA). The UV-VIS spectrum measurement was performed using a JASCO V-670 Spectrophotometer. The solar cell measurement was performed, using a Keithley 4200 source meter and a solar simulator under 100 mWcm⁻² AM 1.5G in air (Bunkoukeiki CEP-2000SRR). The measured area was fixed to be 0.1 cm² with a non-reflective metal mask. The IPCE spectra were recorded using a monochromatic Xenon lamp (Bunkoukeiki CEP-2000SRR). The impedance spectroscopy is performed using Paios 4.0 Measurement Instrument (FLUXiM AG, Switzerland) with amplitude of 0.1 mV and the frequency is sweep from 5 MHz to 1 Hz at 0 V under dark. The atomic force microscopy images were obtained using a scanning probe microscope (JSPM-5200).

3. Results and discussion

The structure of the SnGe-perovskite solar cell is shown in Fig. 1 with the following configuration of glass / TCO / PEDOT:PSS / Perovskite / C₆₀ / BCP / Ag / Au. Figure 2 shows the J-V curves of the solar cells prepared on different TCO substrates. For each condition, we fabricated 15 different devices to check for the reproducibility. Table 1 summarizes the parameters for the best device for each condition. In the case of FTO with texture substrate, the highest power conversion efficiency achieved is 9.24%, followed by 8.16% for Flat FTO substrate and finally 7.72% for ITO substrate. Figure 3 shows...
Fig. 1. Structure of SnGe-perovskite solar cell fabricated in this study.

Fig. 2. I-V curves for SnGe-perovskite solar cells with various TCO glass.

Table 1. Photovoltaic performance of the best performing devices by using Flat ITO, Flat FTO, and FTO with texture as electrode.

|          | η [%] | FF [-] | Jsc [mA/cm²] | Voc [V] |
|----------|-------|--------|--------------|---------|
| Flat ITO | 7.72  | 0.72   | 19.54        | 0.55    |
| Flat FTO | 8.16  | 0.73   | 20.82        | 0.53    |
| FTO with texture | 9.24  | 0.74   | 22.92        | 0.54    |

the relationship of the device parameters with different TCO substrates. The increase in efficiency when FTO substrate is used is due to the improvement in the FF, Jsc, and Rs. However, the highest Voc is achieved with ITO substrate. As can be seen from Fig. 2, the device variation is smallest in the case of FTO substrates and highest in the case of ITO substrates.

The reason for the higher Jsc in the case of FTO with texture and Flat FTO compared to Flat-ITO substrate can be related to the substrate transmittance as shown in Fig. 4. The transmittance of FTO with texture and Flat FTO is higher in near IR region which is beneficial in the case of tin-based perovskite due to the broad absorption spectrum of tin-based perovskite reaching 950 nm. This allowed for more photons to be converted into electrons and thus increased the Jsc.

Fig. 3. The relationship between the kind of TCO glass and photovoltaic performances. (a) Efficiency, (b) Voc, (c) Jsc, (d) fill factor, (e) Rs, and (f) Rsh.

Fig. 4. Transmittance spectra of various TCO substrates.

The higher Voc in the case of Flat ITO substrate can be explained from the lower work function of the Flat ITO substrate which is deepest, followed by FTO with texture substrate and finally Flat FTO substrate (Table 2). The Fermi level of PEDOT:PSS is expected to be shifted according to the work function of the metal, in this case is TCO substrate.
This is known as the Fermi level pinning, typical in the case of metal-semiconductor junction. This resulted in the large Fermi level difference of the PEDOT:PSS Fermi level and C_{60} Fermi level and hence leading to higher $V_{oc}$.

**Table 2.** The fermi level and the sheet resistance of various TCO film.

| TCO Film          | Ef [eV] | $\sigma$ [$\text{S cm}^{-2}$] |
|-------------------|---------|-------------------------------|
| Flat ITO          | -4.81   | 4.572                         |
| Flat FTO          | -4.70   | 7.763                         |
| FTO with texture  | -4.72   | 9.205                         |

To establish the relationship between the perovskite strain and the device efficiency, we performed XRD analysis of perovskite layers on the three substrates. Figure 5 shows the XRD spectrum of perovskite thin film deposited on the TCO substrate, where main peaks of the perovskite at 14.3°, 24.7°, 28.5°, 32.0°, 40.6°, and 43.2°, are detected. In addition, the intensities of the perovskite peaks are similar across the three substrates, suggesting the same crystal orientation on the substrates. A Halder-Wagner plot was made from the acquired XRD spectrum (Fig. 5). The obtained plot shows a linear fit where the crystal size is calculated from the slope and the relative crystal strain is calculated from the y-axis intercept (Fig. 6 and Table 3). In the case of Flat FTO, the crystal strain is the smallest among the three substrates, however the efficiency is still lower than FTO with texture substrate as a result of smaller crystal size leading to lower $J_{sc}$. From the XRD result, no clear conclusion can be drawn on the effect of relative strain and grain size on the device performance.

Figure 7 shows the impedance plot of the three types of device to investigate the charge transport within the devices. By using the equivalent circuit, we determined the series resistance and the charge recombination resistance. From the $R_s$, Flat ITO has the lowest resistance followed by Flat FTO and lastly FTO with texture. From the $R_i$ value, we would expect Flat ITO-based devices to have higher $J_{sc}$ due to the lower $R_s$ which could mean better charge injection from the perovskite. However, this is not the case. This could mean that apart from the low $R_s$, there is another factor which has larger effect on the $J_{sc}$. This brings our point regarding the transmittance of the substrates. $R_{rec}$ however shows the same trend as the $V_{oc}$ in which Flat ITO substrate showed the largest value followed by FTO with texture substrate and finally Flat FTO substrate. A high $R_{rec}$ means that charge recombination reaction is suppressed more efficiently.

**Fig. 5.** XRD spectra of Sn-perovskite layer on various TCO substrates.

**Fig. 6.** The Halder-Wagner plot of Sn-perovskite layer on various TCO substrates.

**Table 3.** The crystal strain and crystallite size which are calculated by the Halder-Wagner plot.

| TCO Film          | Crystal strain [%] | Crystallite size [nm] |
|-------------------|--------------------|-----------------------|
| Flat ITO          | 0.209              | 264.5                 |
| Flat FTO          | 0.198              | 255.9                 |
| FTO with texture  | 0.209              | 268.7                 |

Figure 8 shows the AFM image (measurement area: 4 nm $\times$ 4 nm) of the TCO substrate. The surface roughness ($R_q$) of the FTO with texture substrate is 55.4 nm followed by Flat FTO manufactured with of 13.4 nm. In the case of Flat ITO substrate, the surface roughness is extremely low such that we did not manage to get a clear AFM
image (measurement area: 6 nm × 6 nm). We could conclude the surface roughness as follow: FTO with texture > Flat FTO > Flat ITO.

As shown in impedance and sheet resistance, the resistance of the substrate is the lowest for Flat ITO, followed by Flat FTO and FTO with texture (Fig. 5 and Table 2). However, $R_s$ of the output IV curve is the smallest in FTO with texture, and it can not be said that $R_s$ of the device is determined by the conductivity of the substrate itself.

**Fig. 7.** Nyquist plot of the three different devices obtained from impedance spectroscopy measurement under dark.

**Fig. 8.** AFM images of TCO substrate, (a) Flat ITO, (b) Flat FTO, (c) FTO with texture.

4. Conclusion

In this study, we investigated the influence of transparent conductive films on the solar cell characteristics of SnGe-perovskite solar cells. As a conclusion, it is found that the efficiency of the SnGe-perovskite solar cell is highest in the case of FTO with texture substrate with smaller efficiency deviation. We found that the improvement in the $J_{sc}$ is the main factor contributing to the high efficiency. This is due to the higher transmittance of FTO with texture substrate which could allow more light to be absorbed by the perovskite layer. However, the $V_{oc}$ is slightly lower than that if Flat ITO substrate which originated from the deeper work function of Flat ITO substrate. Despite the difference in the surface roughness, the crystal size and the relative strain did not affect the performance as much as the substrate’s transmittance and work function. This work will provide a basis of fabricating higher efficiency solar cells while keeping the fabrication cost low.

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