Strategies to Fabricate Flexible SnO$_2$ Based Perovskite Solar Cells Using Pre-Crystallized SnO$_2$

Detao Liu$^1$, Hao Chen$^1$, Yameen Ahmed$^1$ and Shiban Li$^{1*}$

$^1$ State Key Laboratory of Electronic Thin Films and Integrated Devices, and School of Optoelectronic Science and Engineering, University of Electronic Science and Technology of China (UESTC), Chengdu, Sichuan 610054, China

$^*$ Corresponding authors, Shiban Li, email, shibanli@uestc.edu.cn.

Abstract. Perovskite solar cells (PSCs) have attracted much attention since the first report. Flexible PSCs are one of the important development orientations due to its lightweight. However, a low temperature process is essential to fabricate the flexible PSCs due to the deformation of the plastic substrate. Here, the pre-crystallization SnO$_2$ colloids have been used to deposit the electron transport layer of flexible PSCs. The photovoltaic performance of flexible PSCs has been optimized through controlling the annealing temperature and SnO$_2$ thickness. A moderate annealing temperature reduces the deformation of flexible substrates and protects the conductive layer. A SnO$_2$ film with a suitable thickness not only blocks the direct contact between perovskite and electrode, but also transports the electron from perovskite to anode efficiently. As a result, the power conversion efficiency of the champion PSCs has been improved to 11.61%.

1. Introduction

The perovskite with ABX$_3$ structure (A=Cs, methylammonium (MA), formamidinium (FA); B = Pb, Sn; X = Cl, Br, I) has attracted a lot of attention since it has been used the light-harvester of solar cells [1-2]. The highest reported power conversion efficiency (PCE) of perovskite solar cells (PSCs) has exceeded 23% [2-3].

Flexible PSCs are one of the important development orientations due to its lightweight. Electron transport layer (ETL) is a vital layer for PSCs. It not only transports electrons to cathode but also blocks holes to recombine with electrons in cathode. Titanium dioxide (TiO$_2$) has been widely used as the ETL in most PSCs [4-9]. However, TiO$_2$ need be annealed at the high temperature of 400-500°C to form a favorable crystallization, resulting in a limitation in flexible PSCs. To avoid the high-temperature annealing process, some other acceptor-type materials such as PCBM, ZnO, SnO$_2$ and Nb$_2$O$_5$, have been developed as the ETL materials. [1-10]. Although this materials have lower the annealing temperature below 200°C, most of them used as ETL still need be annealed at more than 120°C which is higher than the deformation temperature of flexible substrates. The dilatation coefficients of flexible substrate is much higher than that of the upper transport conductive oxide (TCO), resulting in the fragmentation of TCO likely when the substrate is heated at a high temperature. PCBM is an expensive material and it can increase the fabrication cost of perovskite solar cells (PSCs). It is very meaningful to find a new cheap ETL material without high-temperature annealing process. So many researchers have done a lot of works on low temperature ETL materials. Liu et al. used solid-state ionic-liquid (1-benzyl-3-methylimidazolium chloride) as the ETL material for flexible PSCs.
has decreased the annealing temperature to 70 °C, which is favorable for fabrication of flexible PSCs. They finally obtained flexible PSCs with a PCE of 16.09 % which was the highest reported PCE for flexible PSCs at that time [11]. Zhan et al. developed a fused-ring electron acceptor based on indacenodithiophene (IDIC) as the ETL for planar PSCs. The annealing temperature for IDIC film was also 70 °C and the IDIC based PSCs showed a champion PCE of 19.1 % which was higher than the reference PSCs based on TiO₂ [12]. Some metal oxide deposited by vapor based deposition methods also has lower the prepare temperature below 100 °C. Fang et al. used a pulse laser deposition method to deposit SnO₂ films at room temperature and the room-temperature SnO₂ (RT-SnO₂) based PSCs showed a PCE of 17.29 %. The flexible PSCs based on RT-SnO₂ yielded a highest PCE of 14.0 % [13]. Yan et al. used plasma enhanced atomic layer deposition to deposit SnO₂ film as ETL for PSCs [14].

In this work, we report using SnO₂ nanocrystal colloidal disperse solution to deposit ETL of flexible PSCs. The annealing temperature of the ETL has been explored first to obtain the optimized annealing temperature. Then, the coverage change of SnO₂ layer on TCO with the deposition frequency is investigated. It is found that the flexible substrate start to deform at the temperature higher than 120 °C, which deteriorates the photovoltaic performance of the flexible PSCs. The coverage of SnO₂ films on TCO is complete when the deposition frequency excesses 3. Owing to the low-temperature process and complete coverage, the flexible PSCs achieve a PCEs of 11.64 %.

2. Experimental
The indium tin oxide on Polyethylene naphthalate two formic acid glycol ester (ITO-PEN) substrates were cleaned in absolute ethyl alcohol in ultrasonic bath for 15 minutes. After ITO PEN substrates were cleaned by the UV-Ozon treat for 20 minutes, a SnO₂ film was deposited by spin-coating diluted SnO₂ nanoparticles colloidal solution (Alfa Aesar (tin(IV) oxide, 15% in H₂O colloidal dispersion)) according to Reference [2]. After the spin-coating, the SnO₂ film was heated at 100 °C for 0.5 h. Then the substrates were treated with the UV-Ozone again and transferred into the glovebox. Perovskite films were prepared by spin-coating with a speed of 1000 rpm for 10 s and 5000 rpm for 45 s. At 9 s before the ending of spin-coating program, 150 μL chlorobenzene was dropped onto the spinning substrate. Then, the perovskite films were heated at 100 °C for 60 min. The perovskite solution was prepared as following. 507 mg PbI₂, 73.4 mg PbBr₂, 172 mg FAI and 22.4 mg MABr was dissolved into 1 mL solvent mixture (V(dimethylsulfoxide (DMSO)) ,V(Dimethyl Formamide (DMF))=3 ,7) to prepare the solution 1. Then 52 μL CsI solution (390 mg in 1 mL DMSO) was added into the solution 1 and then the final solution was stirred for 2 hours. The HTL was prepared by spin-coating the HTL solution at 5000 rpm for 30 s. The HTL solution was prepared by dissolving 72.3 mg 2,29,7,79-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene (spiro-MeOTAD), 28.8 ml 4-tert-butylpyridine, 17.5 ml of a stock solution of 520 mg/mL lithium bis(trifluoromethylsulphonyl)imide in acetonitrile and 29 ml of a solution of 300mg/ml FK209 in acetonitrile in 1 ml chlorobenzene. Finally, 100nm of Au top electrode was thermally evaporated onto the HTL.

The current density-voltage (J-V) characteristic of PSCs was recorded by Keithley source unit 2400 under AM 1.5G sun intensity illumination by a solar simlulator from Newport Corp. The scanning electron microscope (SEM) was conducted on field emission fitting SEM (FEI-Inspect F50, Holland). The transparency was measured using Shimadzu 1500 spectrophotometer.
3. Results and discussion

3.1. Impact of annealing temperature on photovoltaic performance

The first step to optimize the photovoltaic performance of flexible PSCs is exploring the affection of annealing temperature on flexible substrates. The PEN substrate and ITO have different thermal expansion coefficients. A high temperature annealing process can induce the cracks. The ETL materials can fill the crack when the substrates are annealing, resulting in a lower conductivity in ITO films. To identify how the annealing temperature affects the photovoltaic performance, the conductivity of substrates heated at different temperature was measured. The deformation of flexible substrates heated at different temperature are shown in Figure 1(a). The measurement is carried on simple devices with a structure of Ag/ITO/Ag. However, there is no distinct difference in the conductivity of substrates heated at different temperature. All the resistance values are at the range of 9-10 Ω. Although the ITO-PEN deformed, the ITO can connect to each other again and cracks in ITO can disappear due to the absent of SnO\textsubscript{2} nanoparticles.

To obtain the optimal annealing temperature, the flexible PSCs based on SnO\textsubscript{2} annealed at different temperature were prepared and the photovoltaic performance was characterized through measuring the J-V curves. The J-V curve of best-performance device in each group is shown in Figure 1(b) and the corresponding photovoltaic parameters are listed in Table 1. When the annealing temperature reaches 160 °C, the highest PCE of flexible PSCs is lower than 2 %. The PCE increase dramatically through reducing annealing temperature of SnO\textsubscript{2}. 100 °C is the optimal annealing temperature for the flexible PSCs. The champion flexible PSCs achieves a PCE of 9.55 %. From the photovoltaic performance, the annealing with a temperature more than 140 °C results in an inferior photovoltaic performance. However, there is no difference in the conductivity of the ITO heated at different temperature. We speculate that the SnO\textsubscript{2} fills the cracks when the cracks appear at the high-temperature annealing step, so the conductivity of ITO drops dramatically, as shown in Figure 1(c).

![Figure 1](image)

**Figure 1.** (a) Photographs of flexible substrates heated at different temperature, (b) J-V curves of flexible PSCs based on SnO\textsubscript{2} heated at different temperature, (c) schematic diagram of how annealing temperature of SnO\textsubscript{2} affects photovoltaic performance of flexible PSCs.

**Table 1.** Photovoltaic parameters of flexible PSCs based on SnO\textsubscript{2} heated at different temperature

| Device          | J\textsubscript{SC} (mA/cm\textsuperscript{2}) | V\textsubscript{OC} (V) | FF (%) | PCE (%) |
|-----------------|-----------------------------------------------|-------------------------|--------|---------|
| PSCs based on 100-SnO\textsubscript{2} | 16.96                                         | 0.98                    | 57.46  | 9.55    |
| PSCs based on 120-SnO\textsubscript{2} | 15.64                                         | 0.96                    | 57.61  | 8.65    |
| PSCs based on 140-SnO\textsubscript{2} | 11.15                                         | 0.57                    | 38.23  | 2.43    |
| PSCs based on 160-SnO\textsubscript{2} | 15.33                                         | 0.25                    | 29.75  | 1.14    |
3.2. Impact of SnO\textsubscript{2} coverage on photovoltaic performance

After the optimal annealing temperature was obtained, the thickness of the SnO\textsubscript{2} was also optimized. The thickness of SnO\textsubscript{2} layer affects the coverage of the ETL on TCO. A thin SnO\textsubscript{2} film can't cover the TCO completely, resulting in the direct contact between perovskite and TCO. The direct contact between perovskite and TCO induces the serious recombination and deteriorates the photovoltaic performance. However, if the coverage is complete, the increasing thickness of SnO\textsubscript{2} can lead to a inferior conductivity, which also is not favoured for the high-performance flexible PSCs. The thickness of SnO\textsubscript{2} was adjusted by controlling the frequency of the spin-coating process. To identify the coverage of ETL on TCO, the surface morphology of ETL has been characterized by using SEM methods and the results are shown in Figure 2 (a-d). Some humps on the surface of bare ITO-PEN were identified and the humps induced the incomplete coverage of SnO\textsubscript{2}. After the first layer of SnO\textsubscript{2} were spin-coated onto the ITO-PEN, some bare ITO humps still existed and a lot of small white particles appeared on the surface. The bare ITO humps indicated the SnO\textsubscript{2} didn't cover the ITO completely, and the white particles were introduced from the SnO\textsubscript{2} colloid solution. After the second spin-coating and the third spin-coating, the humps almost disappeared and the films showed much smoother, indicating the ITO were covered by ETL completely. Figure (e-f) has shown the coverage variation with the thickness of ETL.

The transmittance of the ITO-PEN with/without SnO\textsubscript{2} layer and ITO-Glass has also been characterized here, as shown in Figure 3(a). Compared with the ITO-Glass, the ITO-PEN has a much lower transmittance, and the light at wavelength range of 300-380 nm can't penetrate the PEN substrate. After the deposition of the SnO\textsubscript{2} layer, the transmittance became lower slightly. The low transmission of the light can result in a low current. Hence, a suitable thickness of SnO\textsubscript{2} is vital to the photo-generated current.

The flexible photovoltaic devices with different thickness of ETL have been fabricated here. The thickness of the SnO\textsubscript{2} layer has been adjusted by controlling the deposition frequency. The current density-voltage (J-V) curves of flexible PSCs based on SnO\textsubscript{2} with different thickness are shown in Figure 3(b), and the corresponding photovoltaic parameters are listed in Table 2. The photovoltaic performance statistic data are also shown in Figure 3(c). To simplify the expression, we used xL-SnO\textsubscript{2}
to represent the SnO$_2$ layer with different deposition frequencies. The flexible device with 3L-SnO$_2$ yield the highest PCE of 11.62 %. From the statistic data, the optimal thickness of ETL is obtained through spin-coating SnO$_2$ solution on ITO-PEN 3 times. The reproducibility of the devices became better as the thickness increased. The better photovoltaic performance of flexible PSCs based on 3L-SnO$_2$ is resulted from the complete coverage of ETL on ITO. However, increasing the thickness of SnO$_2$ decrease the conductivity of ETL and induce a inferior photovoltaic performance.

![Figure 3](image)

Table 2. Photovoltaic parameters of flexible PSCs based on SnO$_2$ with deposition frequency

| Device                  | $J_{SC}$ (mA/cm$^2$) | $V_{OC}$ (V) | FF (%) | PCE (%) |
|-------------------------|-----------------------|--------------|--------|---------|
| PSCs based on 1L-SnO$_2$| 16.89                 | 1.01         | 57.86  | 9.87    |
| PSCs based on 2L-SnO$_2$| 16.46                 | 0.96         | 68.92  | 10.89   |
| PSCs based on 3L-SnO$_2$| 17.40                 | 0.96         | 69.50  | 11.61   |
| PSCs based on 4L-SnO$_2$| 16.58                 | 0.98         | 62.31  | 10.10   |

4. Conclusion

In summary, the flexible PSCs based on SnO$_2$ was developed through optimizing the annealing temperature and thickness of SnO$_2$ films. A moderate annealing temperature of 100 °C suppressed the deformation of flexible substrate and guarantee the electrical properties of PSCs. The thickness of SnO$_2$ is also vital to the photovoltaic performance of flexible PSCs. A thin SnO$_2$ can't cover the rough ITO layer completely and a thick SnO$_2$ can introduce a inferior conductivity. The optimized thickness of SnO$_2$ films was obtained via spin-coating SnO$_2$ colloid disperse solution for 3 times. As a results, the flexible PSCs yield the champion PCE of 11.61 %. Further efficiency improvements are expected through improve the transmittance of flexible substrates.

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