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Abstract

Perovskite solar cells (PSCs) have recently become a major research field for solar cell technologies. The power conversion efficiency (PCE) of the lab-scale perovskite solar cell has been substantially improved in the last few years, and some groups have already reported PCE values above 25%. The performance of the PSCs depends on various factors, including the structure, composition, and morphology of the perovskite film, the architecture of the device, and the optoelectronic properties of the charge transporting layers. Therefore, optimization of the fabrication of each layer is essential to obtain efficient cells. In this study, solution-based PSC production was optimized using two different perovskite compositions and two different electron transporting layers. Firstly, TiO₂ based mesoscopic PSCs were fabricated with MAPbI₃ and Cs₈(0.05)FA₀.₈₅MA₀.₁₅PbI₂(2.₇)Br₀.₃ perovskite films. The PCE of the best performing cell with FTO/c-TiO₂/m-TiO₂/Cs₈(0.05)FA₀.₈₅MA₀.₁₅PbI₂(2.₇)Br₀.₃/Spiro-OMeTAD configuration was determined as 17.0% and Voc of 1.10 V, Jsc of 23.38 mA/cm², FF of 0.66, while the PCE of the MAPbI₃ based cell was only 6.6% with Voc of 0.93 V, Jsc of 18.40 mA/cm², and FF of 0.38. The difference in the PCE values was attributed to the different morphology of the perovskite layers in each cell. Secondly, the c-TiO₂/m-TiO₂ electron transporting layer was replaced with SnO₂ to fabricate planar PSCs. These cells displayed an efficiency of 15.06% with the corresponding photovoltaic parameters; Voc 1.091 V, Jsc 22.63 mA/cm², and FF 0.54. This current study sheds light on how to achieve high efficiency for solution-based perovskite solar cells.

Keywords: MAPbI₃; Mixed cation; SnO₂ ETL; TiO₂ ETL

1. Introduction

Among the third-generation solar cells, PSCs appear as one of the most promising photovoltaic technologies due to their high efficiency, easy fabrication, and low-cost
production (Fan et al., 2015). A typical perovskite solar cell consists of hole and electron charge-transporting layers, a perovskite layer, and electrodes (Kim et al., 2020). Briefly, the cell functions by the absorption of the incident light through the perovskite layer and then extraction/transportation of the photogenerated holes and electrons from this layer by the corresponding charge-transporting layers (Mora-Seró, 2018).

Morphology and composition of the perovskite layer play an essential role in determining the performance of these cells (Li et al., 2018; Ono et al., 2017). Up to now, various methods have been developed and used in the production of the perovskite layers with large and uniform grains (Tailor et al., 2020). Among these, the solution-based spin coating has attracted much attention due to its simplicity and low cost (Vaynzof, 2020). Spin coating of the perovskite precursor has been carried out by the following two different approaches, i.e., one-step and two-step methods (Wang et al., 2018). All precursors are dissolved in a suitable solvent for the former approach and then spin coated on the substrate at a single deposition step. This is advantageous in terms of processing, but the application of an antisolvent is necessary to induce crystallization of the perovskite phase (Li et al., 2017). For the latter, the perovskite layer is achieved by the deposition of the second group of precursors (e.g., methylammonium iodide, MAI) following the first one (e.g., lead iodide, PbI2). It is worth noting that this was the preferred approach for the initial studies, but then the one-step approach became popular after optimization of the antisolvent application (Xiao et al., 2014).

It is known that the optoelectronic properties of the perovskite layer can be modified by compositional engineering. In the case of one-step spin coating, the perovskite composition can be controlled easily by adjusting the molar ratios of the constituent species in the precursor solution. Up to now, most of the efficient solar cells have been fabricated using multiple cations and a mixed halide perovskite layer (Jung et al., 2019; Kim et al., 2020). Besides the morphology and composition of the perovskite layer, the optoelectronic features of the charge transporting layers strongly impact the efficiency of the cell (Le Corre et al., 2019). Traditionally, TiO2 and 2,2′7,7′-tetrakis(N,N-di-p-methoxyphenyl amine)-9,9′-spirobifluorene (spiro-MeOTAD) have been employed as the electron and hole transporting layers (ETL, HTL), respectively (Kaya et al., 2021; Mahmood et al., 2017). Although the highest efficiency PSCs have been obtained using TiO2 as the ETL, SnO2, which has proper conduction band alignment with perovskite, high electron mobility, and wide bandgap, has attracted attention as an alternative to TiO2 (Jiang et al., 2018). Moreover, SnO2 based cells can be fabricated on flexible substrates due to low-temperature processing (150 °C) and exhibit a more negligible hysteresis effect compare to TiO2 based cells (Liu et al., 2019; Yu et al., 2020).

As can be seen from the above-mentioned literature, many factors affect the performance of the PSCs. Therefore, optimization of the fabrication of each layer is essential to obtain high-efficiency cells. In this study, PSC fabrication was tried to be optimized using the solution-based one-step approach. Two different perovskite compositions (MAPbI3 and Cs0.05FA0.85MA0.1PbI2(2.7)Br(0.3)) were studied on the TiO2 layer by employing identical deposition conditions. The effect of the composition on the structural, morphological, and optical properties of the perovskite film and the performance of the cell were investigated in detail. Furthermore, planar PSCs were fabricated using SnO2 as an ETL and compared with the mesoscopic TiO2 based cells.
2. Methods

2.1 Fabrication of the perovskite solar cells

Perovskite solar cells were fabricated using the device configurations as given schematically in Fig. 1. Fluorine-doped tin oxide (FTO) glass substrates (Sigma Aldrich, 7 \( \Omega \) sq), patterned by etching with zinc powder and 2M HCl acid, were cleaned by de-ionized water, acetone, ethanol, and treated by UV-ozone, respectively. Compact TiO\(_2\) (c-TiO\(_2\)) and mesoporous TiO\(_2\) (m-TiO\(_2\)) as ETLs were deposited on FTO by aerosol spray pyrolysis and spin coating techniques, respectively. In aerosol spray pyrolysis, titanium diisopropoxide bis(acetylacetonate) (75\% in 2-propanol) was diluted in ethanol and then sprayed on the substrates preheated to 450 °C, using oxygen as the carrier gas. After that, diluted TiO\(_2\) paste (30NRD, Dyesol, TiO\(_2\)/ethanol:1/6, w/w) was coated on the c-TiO\(_2\) at 4000 rpm for 20 s using spin coating and annealed at 450 °C for 30 min in air. In the case of SnO\(_2\) deposition as ETL, Alfa Aesar SnO\(_2\) dispersion solution (15 wt\% in H\(_2\)O) was used. Prior to deposition, dispersion solution was diluted in de-ionized water at a volumetric ratio of 1:8 and then spin-coated at 4000 rpm for 30 s on the pre-cleaned FTO substrates. Thereafter, SnO\(_2\) films were annealed at 150 °C for 30 min in air. Perovskite solutions for each composition were prepared by dissolving 1.35 M PbI\(_2\) and 1.35 M MAI for MAPbI\(_3\) and 0.07 M CsI, 1.12 M FAI, 0.15 M MABr, 1.23 M PbI\(_2\), and 0.15 M PbBr\(_2\) for (CsFA)\(_2\)Pb(1Br)\(_3\) in dimethylformamide/dimethylsulphoxide (4:1, v/v). Then the corresponding perovskite layers were deposited on ETLs by one-step spin coating using a two-step program, i.e., 2000 rpm for 10 s, followed by 6000 rpm for 30 s in a nitrogen-filled glovebox. During the second step, 200 µL of chlorobenzene was poured on the substrate in the last 10 s as an antisolvent. The samples were then heated at 100 °C for 1 h on a hotplate in the glovebox. After cooling the films down to room temperature, spiro-OMeTAD was coated on the perovskite layers as the HTL (Akin et al., 2019). Finally, the devices were completed by thermal evaporation of 100 nm gold.

**Figure 1:** Schematic illustration of the (a) TiO\(_2\) based mesoscopic, (b) SnO\(_2\) based planar PSCs

2.2 Characterization

The crystal structure and phase contents of the as-synthesized perovskite films were determined by X-ray diffraction. XRD measurements were carried out using a Bruker D8 Advance diffractometer operating at 40 kV and 40 mA with Cu-K\(_\alpha\) (\( \lambda = 1.5406 \) Å) radiation. The UV-Vis absorbance spectra of the films were recorded using Shimadzu ISR-2600...
spectrophotometer. The microstructural features were investigated using Hitachi SU-5000 Field Emission Scanning Electron Microscopy (FE-SEM). The current density–voltage (J–V) curves of PSCs were recorded using Keithley 2400 semiconductor characterization system equipped with an OAI Class AAA solar simulator under AM 1.5 G illumination of 100 mW/cm² as the light source. All measurements were carried out using a non-reflective metal mask with an aperture area of 0.16 cm².

3. Results and Discussion

XRD patterns of as-deposited MAPbI₃ and Cs₈(0.05)FA₄(0.85)MA₅(0.1)PbI₂(2.7)Br₀(0.3) films on FTO/c-TiO₂/m-TiO₂ layers are presented in Fig. 2 (a) and (b), respectively. In Fig. 2(a), all the diffraction peaks can be indexed as MAPbI₃ in tetragonal structure (ICSD: 238610) except the peaks that belong to the FTO substrate (denoted by a reverse triangle). It is obvious that the MAPbI₃ layer is polycrystalline and possesses (220) as the preferred orientation. On the other hand, XRD pattern in Fig. 2(b) revealed that the Cs₈(0.05)FA₄(0.85)MA₅(0.1)PbI₂(2.7)Br₀(0.3) crystallizes in cubic structure. The peaks in the pattern are all matched with ICSD: 250736 for FA-PbI₃. In addition to the peaks of FA-PbI₃, diffraction peaks belonging to TiO₂ (denoted by a closed circle) and FTO (denoted by a reverse triangle) located under the perovskite layer were identified. No impurity phase was detected in both patterns.

![Figure 2: XRD patterns of (a) MAPbI₃ and (b) Cs₈(0.05)FA₄(0.85)MA₅(0.1)PbI₂(2.7)Br₀(0.3) films on FTO/c-TiO₂/m-TiO₂ layers](image)

The optical properties of the perovskite films were investigated by UV-Vis spectroscopy. The absorbance spectra of the MAPbI₃ and Cs₈(0.05)FA₄(0.85)MA₅(0.1)PbI₂(2.7)Br₀(0.3) films are shown in Fig. 2(a) and (b), respectively. Both perovskite films exhibited strong absorption in the visible region. The absorption edge of MAPbI₃ and Cs₈(0.05)FA₄(0.85)MA₅(0.1)PbI₂(2.7)Br₀(0.3) were at ~778 nm and 765 nm, corresponding to a direct bandgap energy of 1.59 eV and 1.62 eV, respectively.
It is well known that the effect of A-site cations on the optical properties of the perovskite (APbI$_3$) phase is subsidiary (Kim et al., 2020). For example, band gaps of perovskites with various A-cations, including FAPbI$_3$, MAPbI$_3$, and CsPbI$_3$ were reported as 1.48, 1.58, and 1.74 eV, respectively (Eperon et al., 2015; Eperon et al., 2014). On the other hand, the X-site anion can significantly modify the optical properties of the perovskite phase depending on the ionic radius of the halide anions. As an example, the bandgap of MAPbI$_3$ can be increased from 1.58 eV to 2.28 eV if all I$^-$ ions (the ionic radius:220 pm) present in the composition are replaced with Br$^-$ ions (ionic radius:196 pm)(Noh et al., 2013). In this study, it was observed that the bandgap of Cs$_{(0.05)}$FA$_{(0.85)}$MA$_{(0.1)}$PbI$_{(2.7)}$Br$_{(0.3)}$ was slightly higher than that of the MAPbI$_3$. Both perovskite phases had suitable bandgap values for photovoltaic applications in accordance with the values reported in the literature.

**Figure 3:** UV-Vis absorbance spectrum of the (a) MAPbI$_3$ and (b) Cs$_{(0.05)}$FA$_{(0.85)}$MA$_{(0.1)}$PbI$_{(2.7)}$Br$_{(0.3)}$ films. The $\alpha h\nu^2$-$h\nu$ plots for (c) MAPbI$_3$ and (d) Cs$_{(0.05)}$FA$_{(0.85)}$MA$_{(0.1)}$PbI$_{(2.7)}$Br$_{(0.3)}$ films

The microstructural properties of spin-coated MAPbI$_3$ and Cs$_{(0.05)}$FA$_{(0.85)}$MA$_{(0.1)}$PbI$_{(2.7)}$Br$_{(0.3)}$ films were investigated by FE-SEM. The as-deposited surface
morphism of these films is presented in Fig. 3 (a) and (b), respectively. It is obvious from these two images that the MAPbI$_3$ and Cs$_{0.05}$FA$_{0.85}$MA$_{0.1}$PbI$_{2.7}$Br$_{0.3}$ phases preferred very different morphologies during the film formation on the c-TiO$_2$/m-TiO$_2$ layers. MAPbI$_3$ formed in the form of an unattached pillar-like morphology, Fig 3(a). As a result, large voids developed between these pillars. This kind of morphology may be attributed to the very fast island-like nucleation and high growth rate of {220}. On the contrary, Cs$_{0.05}$FA$_{0.85}$MA$_{0.1}$PbI$_{2.7}$Br$_{0.3}$ films, deposited under identical conditions, exhibited a favourable morphology which consists of large (~250 nm) and uniform grains, Fig. 3(b). This is desirable to achieve perovskite solar cells with high efficiency. These observations clearly revealed that the nucleation and growth of the perovskite phase and its final morphology are highly dependent on the preferred compositions.

Figure 4: FE-SEM images of (a) MAPbI$_3$ and (b) Cs$_{0.05}$FA$_{0.85}$MA$_{0.1}$PbI$_{2.7}$Br$_{0.3}$ films

After the structural, optical, and morphological characterization of MAPbI$_3$ and Cs$_{0.05}$FA$_{0.85}$MA$_{0.1}$PbI$_{2.7}$Br$_{0.3}$ films, we have fabricated several PSCs using these two phases with the following device configuration; FTO/c-TiO$_2$/m-TiO$_2$/perovskite/spiro-MeOTAD/Au and compared their photovoltaic characteristics. The J-V curves (reverse scan, 1.2 V to -0.2 V) of the best performing PSCs are shown in Fig. 4.
Figure 5: The J-V curves of the PSCs fabricated with MAPbI$_3$ and Cs$_{0.05}$FA$_{0.85}$MA$_{0.1}$PbI$_{2.7}$Br$_{0.3}$ films

The cell having the Cs$_{0.05}$FA$_{0.85}$MA$_{0.1}$PbI$_{2.7}$Br$_{0.3}$ phase exhibited an open-circuit voltage ($V_{oc}$) of 1.10 V, a short-circuit current density ($J_{sc}$) of 23.38 mA/cm$^2$, and a fill factor (FF) of 66%; thus, a power conversion efficiency (PCE) of 17.0% was achieved. On the other hand, the PCE of the cell based on the MAPbI$_3$ phase was determined as 6.6% with $V_{oc}$, $J_{sc}$, and FF of 0.93 V, 18.40 mA/cm$^2$, and 38%, respectively. The low PCE of the cell with MAPbI$_3$ phase is not surprising due to the formation of large voids in this layer, as already revealed by FE-SEM examinations, which are probably forming shunt paths by inducing direct contact of electron and hole-transporting materials (Adjokatse et al., 2019). As a result, the $V_{oc}$ and FF of the cells are reduced substantially. Moreover, the absence of a continuous active layer may decreased the amount of adsorbed photons, which is responsible for the low $J_{sc}$ (Agarwal & Nair, 2017).

Finally, we fabricated planar PSCs by replacing c-TiO$_2$/m-TiO$_2$ layer with c-SnO$_2$ to investigate effect of the ETL material and device configuration on the performance of the Cs$_{0.05}$FA$_{0.85}$MA$_{0.1}$PbI$_{2.7}$Br$_{0.3}$ based PSCs. The J-V curves (forward and reverse scans) of the best performing PSCs based on TiO$_2$ and SnO$_2$ are presented in Fig 6. The corresponding photovoltaic parameters are summarized in Table 1.
Figure 6: The J-V curves of the TiO₂ based mesoscopic and SnO₂ based planar PSCs

Table 1: Photovoltaic parameters for the TiO₂ based mesoscopic and SnO₂ based planar PSCs

<table>
<thead>
<tr>
<th>ETL</th>
<th>Scan direction</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt; (V)</th>
<th>J&lt;sub&gt;sc&lt;/sub&gt; (mA/cm²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>Forward</td>
<td>1.03</td>
<td>23.36</td>
<td>46</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>1.10</td>
<td>23.38</td>
<td>66</td>
<td>17.0</td>
</tr>
<tr>
<td>SnO₂</td>
<td>Forward</td>
<td>1.05</td>
<td>22.62</td>
<td>54</td>
<td>12.8</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>1.09</td>
<td>22.63</td>
<td>61</td>
<td>15.0</td>
</tr>
</tbody>
</table>

It is seen that the PCE of the TiO₂ based cell (17%) was higher than that of the SnO₂ based cell (15%). This can be attributed to the mesoscopic structure of the TiO₂ layer, which enhances the electron injection from the perovskite layer to ETL. On the other hand, both cells exhibited better performance for the reverse scans compared to the forward scans. This behaviour is known as J-V hysteresis and the reason for this mismatch between the J-V curves during opposite scans is unclear (Wu et al., 2016). The hysteresis index (HI) of the produced cells were calculated according to the following equation (Yu et al., 2020):
Hysteresis index = \frac{\text{PCE}_{\text{reverse}} - \text{PCE}_{\text{forward}}}{\text{PCE}_{\text{reverse}}} \times 100 \quad (1)

Hysteresis indexes were determined as 14% and 35% for the SnO$_2$ and TiO$_2$ based cells, respectively. It is believed that charge carrier and defect state accumulations at the perovskite/ETL (or perovskite/HTL) interface is one of the reasons for hysteresis formation (Wu et al., 2016). Therefore, trap-state density at the interface of electron transporting layer and the perovskite film plays a crucial role in the J-V hysteresis formation. Yu et al. (2020) reported that SnO$_2$ possesses a deeper conduction band with lower trap-state density than that of TiO$_2$, which facilitated faster charge extraction resulting in hysteresis-free PSC. As compared the literature, the SnO$_2$-based cells have displayed much lower hysteresis index than that of the cells with TiO$_2$.

Figure 7: The statistical photovoltaic parameters of TiO$_2$ based mesoscopic and SnO$_2$ based planar PSCs

In order to investigate the reproducibility, eight cells were fabricated in each configuration. The statistical results of the photovoltaic parameters ($V_{oc}$, $J_{sc}$, FF, PCE) are shown in Fig 7. The PCE were found to be in the range of 15-17% and 12-15% for the TiO$_2$ and SnO$_2$ based cells, respectively. Moreover, all the photovoltaic parameters showed relatively similar variations for both configurations.
4. Conclusion

This study was carried out for the optimization of PSC fabrication by the one-step spin coating method. Two perovskite compositions; i.e., MAPbI₃ and Cs₀.₀₅FA₀.₈₅MA₀.₁PbI₂₇Br₀.₃ were deposited on the FTO/c-TiO₂/m-TiO₂ substrate using identical conditions. XRD analysis indicated that perovskite compositions were produced successfully in polycrystalline structure and free from impurity phases. Both perovskite compositions exhibited similar optical properties. The direct bandgap values were estimated to be 1.59 and 1.62 eV for the MAPbI₃ and Cs₀.₀₅FA₀.₈₅MA₀.₁PbI₂₇Br₀.₃, respectively. FE-SEM analysis revealed that the MAPbI₃ film has formed in pillar-like morphology involving large voids between the individual pillars. On the other hand, Cs₀.₀₅FA₀.₈₅MA₀.₁PbI₂₇Br₀.₃ film had uniform grains with average size of ~250 nm. As a result, PSCs fabricated using MAPbI₃ films displayed lower PCE values than that of the cells with Cs₀.₀₅FA₀.₈₅MA₀.₁PbI₂₇Br₀.₃. The maximum PCE of the cell fabricated using Cs₀.₀₅FA₀.₈₅MA₀.₁PbI₂₇Br₀.₃ film was determined as 17.0% under reverse scan conditions. These findings revealed that the optimization of the perovskite film deposition conditions according to the preferred perovskite composition is a pre-requisite in achieving efficient cells. In order to investigate the effect of the ETL on the performance of the PSCs, c-TiO₂/m-TiO₂ was replaced with SnO₂. For this configuration, the cells exhibited much lower hysteresis on the forward and reverse scans, and the PCE was obtained as 15%. More importantly, reproducibility analyses showed that the difference in the variation of photovoltaic parameters for each configuration is negligible.

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References


