A Novel Nitrogen-Assisted Method for the Perovskite Active Layer Optimization in the Inverted Planar Heterojunction Perovskite Solar Cells

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Abstract. The perovskite solar cells is recognized as a promising candidate for energy industry system because of its tunable band-gap, high absorption coefficient, broad absorption spectrum, high charge carrier mobility and long charge diffusion lengths. However, a dendritic grains morphology, caused by the spin coating procedure, will result in poor coverage and then low power conversion efficiency. In this work, a novel and facile inactive gas assisted method is introduced to obtain uniform and dense perovskite thin films. The dry nitrogen gas blows over the surface of the perovskite solution during the spin-coating process, which promote a faster solvent evaporation. Then, the uniform and compact perovskite film on the substrate was achieved. Typically, the power conversion efficiency (PCE) of the nitrogen gas assisted perovskite solar cells increases from 0.30% to around 9.5%. Furthermore, the favorable start time of nitrogen blowing on devices was also investigated. The PCE stays around 9.46% – 9.78% when the gas starts at 2 sec - 5 sec, and the efficiency decreases to 8.98% if the gas starts at 6 sec. The nitrogen flow assisted method is proved to be an effective way to fabricate dense perovskite films without polluting the environment.

1. Introduction

Organic-inorganic hybrid perovskite materials, applied in the perovskite solar cells, have shown great promise in field-effect transistors, light-emitting diodes, sensors, and photodetectors [1] due to their tunable band-gap, high absorption coefficient, broad absorption spectrum, high charge carrier mobility and long charge diffusion lengths [2]. Recently, the power conversion efficiency (PCE) of lead halide perovskite (CH3NH3PbX3, X = Cl, Br, I) based thin film photovoltaic devices has boost from 3.8% [3] to more than 22.1% [4], [5] in just eight years. The PCE is highly determined by the light-absorbing film’s deposition process which is strongly connected with the morphology and coverage ratio. Usually, perovskite films used in solar cells have been fabricated by a co-evaporation method [6], two-step [7], [8] or one-step [7], [9] solution process. The vapor deposition process is likely to increase the manufacturing cost whereas the sequential two-step deposition procedure will involve a longer overall processing time [10], [11]. The one-step solution deposition is a fast and simple fabrication method but always causes low surface coverage. Xiao et al. developed a fast crystallization-deposition (FDC)
method that involves the spin-coating of a N,N-dimethylformamide (DMF) solution of CH3NH3PbI3 on a substrate, followed immediately by the exposure of the wet film to a second chlorobenzene (CB) solvent to fabricate high quality planar CH3NH3PbI3 thin films, such as full surface coverage, small surface roughness, microscale grain size, and high PCE of 16.2% [10]. Han et al. reported a dissolution-recrystallization method (DRM) with chlorobenzene and dimethylsulfoxide treating the perovskite films during the spin-coating process to control perovskite crystallization and improve the device performance [12]. However, many solvents are poisonous and environmental-unfriendly. Therefore, it is a necessity to develop an alternate method.

Herein, we reported a novel inactive gas (nitrogen gas) assisted technology, which offers the advantage of single-step processing and environmental-friendship. This simple technology involves the spin-coating of a DMF solution of CH3NH3PbI3 on a substrate, followed immediately by exposure of the wet film to a constant nitrogen flow to induce high crystalline single grains. By this new technology, planar heterojunction solar cells yielded a maximum PCE of 9.78% under standard AM 1.5 conditions. We believe this facile method can be applied for the fast production of highly efficient CH3NH3PbI3 based solar cells.

2. Experimental

2.1 Experimental materials
Poly 3,4-ethylenedioxythiophene: poly styrenesulfonate (PEDOT:PSS) and CleviosTM PVP, AI 4083 are purchased from Heraeus Materials Technology Shanghai Ltd. CH3NH3I (MAI) was synthesized via the approach described in the literature [8]. Lead iodide (PbI2, 99%) and Anhydrous N,N-dimethylformamide (DMF, 99.8%) are purchased from Sigma-Aldrich company. [6,6]-phenyl-C61-butyric acid methyl ester (PC61BM, >99%) was purchased from Xi’an Polymer Light Technology Corp. To prepare the perovskite precursor solution, CH3NH3I and PbI2 were mixed in DMF at the molar ratio of 1:1, respectively. The solution was stirred at 60˚C overnight, and was then filtered using 0.45 μm PTFE filters before being used for device fabrication. The concentration of the perovskite precursor solution was 40 wt%.

2.2 Device fabrication
The device structure is shown in Figure 1, starting from the bottom: Glass/ITO substrate, hole transport layer PEDOT:PSS, perovskite photoactive layer, and PC61BM electron transport layer, with a final Ag electrode deposited via thermal evaporation.

Figure 1. Schematic illustration (a) and Cross-sectional SEM image (b) of the designed device.

The device is fabricated according to the previous report [13], [14]. Indium tin oxide (ITO, 15 ohm/sq) glass substrates were cleaned sequentially under ultrasonication for 20 min with detergent, deionized water and isopropyl alcohol. Then PEDOT: PSS films were deposited on the ITO coated glass by spin-coating the PEDOT: PSS solution at a speed of 5000 rpm. After heated at 150 °C on a hot plate for 10 min, the PEDOT:PSS films were mild argon plasma post-treated with PDC-36 G
under a base pressure of around 170 Pa for 3 min. The CH$_3$NH$_3$PbI$_3$ perovskite active layer was deposited onto the as-prepared PEDOT: PSS layer by spin-coating CH$_3$NH$_3$PbI$_3$ precursor solution (40 wt% in DMF) at 4000 rpm for 40 s. In order to improve the crystallization of perovskite active layer deposited by one-step solution method, an additional step was introduced where a 0.4 Mpa dry nitrogen gas flow was blown over the surface of the perovskite solution during the spin-coating process. Then the films were annealed at 110 °C for 30 min inside the glove box filled with nitrogen. After that, a solution of PC61BM in CBZ was spin-coated onto the perovskite films at 3000 rpm for 40 s. Finally, a silver electrode (100 nm) was deposited by thermal evaporation through a shadow mask under a base pressure of 3×10^-4Pa, which defined an active cell area of 0.075cm$^2$.

2.3 Characterization

To improve the measurement accuracy, the J–V curves for all devices were measured by masking the active area with a metal mask. The device photocurrent was measured under an AM 1.5G solar simulator (Japan, SAN-EI, XES-40S1). The current density-voltage (J-V) characteristics for the devices were recorded with a Keithley 2400 source meter and no poling or light soaking process was applied before the J-V measurement. The illumination intensity of the light source was calibrated before the tests by using a standard silicon solar cell with a KG5 filter, which was calibrated by a National Renewable Energy Laboratory (NREL) silicon photo diode, giving a value of 100 mW cm$^{-2}$. All J-V curves reported in this study were measured under a reversed voltage bias. Average values and standard deviations were generated from the measurements of these spots. An X-ray diffractometer (XRD, Philips 1140) with Cu Ka radiation was utilized to compare the crystalline structures of various devices with and without nitrogen assisted. The surface and cross section SEM images were recorded with a FEI Nova dual beam, focused ion beam (FIB), SEM instrument using 5 kV acceleration voltage. Prior to ion beam thinning of the cross section, two platinum protecting layers were deposited in situ using an electron beam source at 6.3 nA and an ion beam source at 0.30 nA. The milling of the cross sections was performed with a gallium ion source at a 52-tilting angle.

3. Results and Discussion

3.1 Procedure of the gas-assisted method

The process of gas assisted method for preparing the CH$_3$NH$_3$PbI$_3$ films is shown in Figure 2. A DMF solution of CH$_3$NH$_3$PbI$_3$ (40wt%) was spin-coated on the PEDOT:PSS layer at 4000 rpm. Compared to the conventional method, a fast nitrogen flow with 0.4 Mpa pressure quickly blew vertically to the substrate.

The role of fast nitrogen flow is to reduce the solubility of CH$_3$NH$_3$PbI$_3$ in the pristine solvent rapidly and thereby promote fast nucleation and growth of the crystals in the film. In contrast, during a conventional spin-coating process where no fast nitrogen flow was involved, the wet film dried slowly and a whitening-gray film was produced. The films were then annealed at 120 °C for 30 min to evaporate any residual solvent and promote crystallization. As shown in Figure 2, the nitrogen gas processed films become darker which indicates the formation of the compact thin film.

![Figure 2. Schematic procedure for the gas-assisted method.](image)
3.2. Effect of gas assisted method on perovskite films

The nitrogen flow that blows over the surface of the CH3NH3PbI3 wet film can promote the solvent evaporation and accelerate the supersaturation of the CH3NH3PbI3 precursor solution. The influence of start time on film properties (the beginning of spin-coating defined as starting time of 0 sec) were tested. Figure 3 shows the SEM images of surface morphology of CH3NH3PbI3 films treated by the nitrogen flow at different start time. It is found that the film prepared by conventional method resulted in a dendritic structure that poorly covers the underlying surface (Figure 3a), while the nitrogen assisted film shows a smoother surface (Figure 3b-e). As the start time varied from 2 to 5 sec, film surface shows dense micro-structure. When the start time increased to 6 sec, the dendritic grain morphology were produced.

In general, the removal of excess precursor solution is a dominant process in the first 2 sec after spin-coating was commenced [15]. The solvent of DMF has high boiling point (153 °C) and low vapor pressure (2.6 mmHg at 20 °C). For the conventional method, slow evaporation results in a low degree of super-saturation, which favors the crystal growth of a small number of existing nuclei, thereby promoting the formation of dendritic perovskite grains [16] (Figure 3a). Whereas, nitrogen flow causes a high degree of super-saturation, the solution is saturated enough to form homogeneous crystallization [17], which can enhance crystallization and prefer-orientation of perovskite crystal (Figure 3b-e). When the time reached 6 sec, the start time is too late that a small number of dendritic grains in random orientation have already been produced (Figure 3f).

![Figure 3. SEM images of the perovskite films made by the nitrogen-assisted method at different start time. (a) untreated, (b) 2 sec, (c) 3 sec, (d) 4 sec, (e) 5 sec, (f) 6 sec.](image-url)

XRD analysis was used to further investigate the influence of blowing start time on the film composition. As shown in Figure 4, there was no obvious difference between 2 and 4 sec, but a clear reduction in the intensity of the CH3NH3PbI3 perovskite diffraction peaks (14.1°, 28.4, 32°) as the start time reaches 6 sec. That indicated a possible change of the grain crystal orientation and granulation of perovskite film, which is consistent with the SEM results.
3.3. The Performance of the devices

Figure 5 shows the photovoltaic parameters of devices fabricated with the nitrogen assisted method. Different start time results in devices with different PCE parameters. The cells show PCEs improvement after nitrogen blowing. However, as the start time is later than 5 secs, the PCEs show a decreasing trend. Uneven coating of perovskite (Figure 3f) causes an uneven coating of the overlaying of PCBM layer. The non-uniform perovskite films exhibited regions with extremely thin coverage of the substrate. In these regions the shunt resistance would be reduced resulting in a lower voltage and fill factor [16]. Therefore, the best start time to produce device with high PCE should be between 2 - 5 sec.

4. Conclusion

In summary, nitrogen assisted method has been developed to fabricate high quality of perovskite films. Compared to the conventional process, this new technique leads to a higher degree of super-saturation resulting the nucleation more favorable that make a uniform perovskite film fully covers the substrate. Furthermore, the gas flow blowing start time from the beginning of spin-coating has also been investigated. When the start time varies between 2 and 5 sec, there are no dendritic grains. The PCE of
perovskite solar cells increased from 0.30% for the pristine CH3NH3PbI3 films based device to 9.78%, 9.55%, 9.37% and 9.46% by the nitrogen-assisted method delayed for 2 sec, 3 sec, 4 sec, 5 sec, respectively. Gas-assisted method is proved to be a useful plan to fabricate dense perovskite film without harm influence to environment.

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