

Novel Cryo-controlled Nucleation Technique for High-efficiency Perovskite Solar Cells

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Abstract

A novel cryo-controlled nucleation technique is developed to grow mixed halide perovskite for solar cells (PSCs). The abrupt decrease in the ambient temperature results in a supersaturation condition in the precursor film prepared by the spin coating process, leading to form uniform nucleation sites for subsequent crystal growth. The low temperature ambient retards the pre-mature crystallization of the perovskite film in the early stage before a uniform seed layer is obtained. This film deposition approach ensures excellent uniformity of the nucleation layers and, subsequently, higher quality perovskite films. A power conversion efficiency (PCE) of 21.4 % for the champion PSC can be achieved by the proposed perovskite growth technique.

Keywords: perovskites; solar cells; nucleation; crystallization

Introduction

The superior photovoltaic properties and low manufacturing cost of PSCs make it highly competitive with the current solar technology such as the dominant crystalline silicon solar cells in the near future. Since the publication of the research work from Jeon *et al.* [1], solvent engineering techniques including the formation of Lewis acid–base adduct in precursor films and introduction of anti-solvent dripping process are the mainstream for preparing solution based mixed halide perovskites with good film morphology, resulting in high performance PSCs. However, there are drawbacks for applying anti-solvent technique for large-scale manufacturing because the morphology of the perovskite films is highly depended on the anti-solvent dripping time, volume and dripping location on the samples. Furthermore, the anti-solvent technique usually works with the spin-coating process. During the spinning process, the anti-solvent can wash away the good solvent in precursor films, leading to supersaturation of precursors, and resulting in rapid nucleation for the subsequent perovskite crystallization [2]. However, the anti-solvent dripping process would be difficult to apply on other large-scale solution processing techniques such as roll to roll processing, slot-die coating and blade coating [3].

We have developed a novel cryo-controlled growth process. Our approach can effectively inhibit the pre-mature crystallization of the perovskites and, thereby, decoupling the nucleation and crystallization phases, which is of significant importance as the failure to do so is the primary cause for the poor-quality perovskite films. We introduce an ultra-low temperature ambient for as-casted precursor layer to freeze the pre-mature reaction of precursors. Meanwhile, the rapid reduction in temperature can lower the solubility of precursors in solvents and the precipitated precursors will form the uniform nucleation sites for subsequent crystallization. A N₂ blow-dry process is also introduced prior to the thermal

annealing step to facilitate the removal of residual solvents in the films. By utilizing the proposed technique, an excellent quality perovskite film can be grown, yielding a PCE of 21.4% with a fill factor of 80 % for a champion PSC.

Experimental

The structure of PSC device and the energy band diagram are shown in Fig. 1. The commercial patterned glass/FTO substrates (7–10 Ω/□) were ultrasonically cleaned by detergent solution followed by deionized (DI) water, acetone, and isopropanol. The electron transport layer (ETL) SnO₂ was prepared on the patterned FTO coated glass by the sol-gel process [4]. The precursors for the synthesis of the mixed halide perovskite include CH₃NH₃I (Dyesol), CH(NH₂)₂I (Dyesol), CH₃NH₃Br (Dyesol), CsI (sigma-aldrich), PbI₂ (sigma-aldrich) and PbBr₂ (sigma-aldrich). The freshly-prepared precursor film by spin-coating process was treated in an ultra-low temperature ambient and the sample was then treated by a pressurized blow-dry process before thermal annealing on a hotplate. The hole transport layer (HTL) was prepared by spin-coating the solution consisting of spiro-MeOTAD (80 mg/mL) in chlorobenzene with additives of Li-TFSI (17.5 μL from the stock solution in a concentration of 520 mg/mL dissolved in acetonitrile) and 29 μL of t-BP. The devices were completed by depositing Au electrodes by thermal evaporation via a shadow mask with a working active area of 0.03 cm². The *I*-*V* characteristics of the devices were measured using a B1500 A semiconductor parameter analyzer under the calibrated Oriol Sol3A solar simulator (Class AAA) equipped with an AM 1.5 filter at 100 mW/cm².

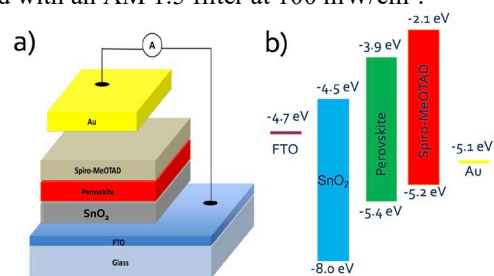


Fig. 1 a) The configuration of the PSC and b) the energy band diagram of the constituent layers of the PSC.

Results and Discussion

The pioneer research works for solution-processed perovskites commonly involved straightforward spin-coating process followed by thermal annealing [5]. In this work, the control samples were prepared by using this conventional method. Figure 2 shows the SEM images for the morphologies of the perovskite films grown by the conventional method (Fig. 2a and 2b) and the cryo-controlled nucleation technique (Fig. 2c and 2d). The quality of the resultant perovskite film is

strongly determined from the uniformity of the seed layer (as-casted precursor film). It is clearly observed from Fig. 2a that the coverage of the as-casted precursor film is very poor. It is not surprising that the resultant perovskite film prepared by the conventional method as shown in Fig. 2b exhibits a large area of uncovered FTO region. As a result, the metal top electrodes of the device come into direct contact with the conductive FTO, leading to form a short circuit. The main reason for the poor quality of perovskite films is attributed to the different solubility of the precursors in the solvent (e.g. DMF), resulting in the different crystal growth rates started from the spin-coating process. While the DMF solvent is evaporating, pre-mature crystallization starts, leading to aggregations of the precursors/perovskite. To retard crystallization until the uniform precursor layer is achieved, the as-casted precursor films are treated in ultra-low temperature ambient. It is noted that all chemical reactions are frozen at the ultra-low temperature and the abrupt reduction in temperature can cause supersaturation of the precursors in the as-casted precursor film and thus induces the formation of homogenous nucleation sites for subsequent crystallization.

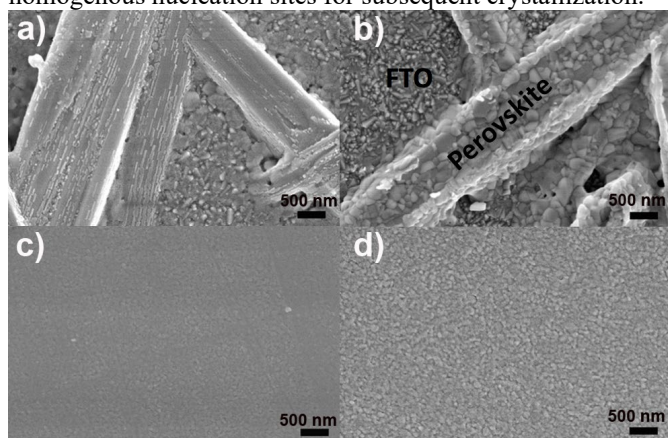


Fig. 2 The SEM images for the comparison of the morphology of the precursor films (a, c) and perovskite films (b, d) prepared by the conventional method (a,b) and cryo-controlled nucleation technique (c, d).

It is noteworthy that the crystallization process is only allowed to take place after the uniform seed layer is achieved. In addition, a N_2 blow-dry process is applied prior to the thermal annealing step to facilitate the evaporation of residual solvents in the precursor films. It is found that if the precursor films trapped with a large amount of solvents, are directly treated by the thermal annealing process, the resultant perovskite films will become very rough and look grey in colour, which is due to re-dissolving the perovskite in the residual solvents and leading to aggregation of the perovskite material. Figure 2c shows the precursor film prepared by the cryo-controlled nucleation technique. A good coverage of precursor seed layer is observed. Figure 2d shows the morphology of the film in Fig. 2c after the N_2 blow-dry treatment and the thermal annealing process. The resultant perovskite film exhibits excellent uniformity without any pinhole, demonstrating the effectiveness of the proposed technique. Figure 3 shows the photothermal deflection spectra (PDS) of the control sample and the sample prepared by the cryo-controlled nucleation technique. The cryo-controlled sample has significantly lower sub-bandgap absorption compared to the control sample. The determined Urbach energy is 23 meV and 21meV for the control and cryo-controlled sample respectively. The obtained

results from PDS clearly indicate that the perovskite film prepared by the cryo-controlled nucleation technique has lower defect density, which is consistent to the observation in SEM.

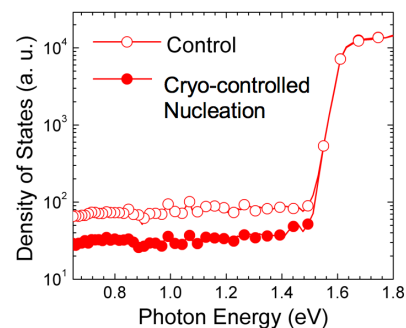


Fig. 3 The PDS spectra for the control and the cryo-controlled sample

With careful optimization of the growth technique, a PCE of 21.4 % with a V_{OC} 1.14 V, J_{SC} 23.5 mA/cm^2 and a fill factor of 80 % can be obtained for the champion PSC.

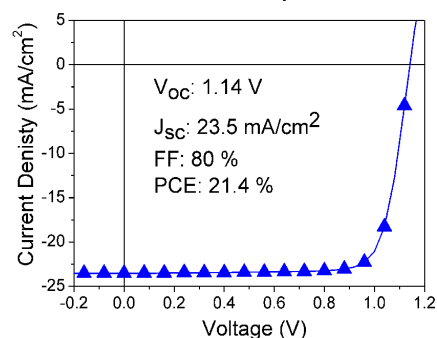


Fig. 4 The I - V characteristics of the champion device based on cryo-controlled nucleation technique

Conclusion

We have demonstrated the cryo-controlled nucleation technique as an effective strategy for synthesizing high quality mixed halide perovskite for PV application. Our proposed method can decouple the nucleation and crystallization phases, which substantially improves the morphology of perovskite films. A PCE of 21.4% can be achieved for the champion PSC based on the proposed technique.

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