



Realizing full coverage of perovskite film on substrate surface during solution processing: Characterization and elimination of uncovered surface



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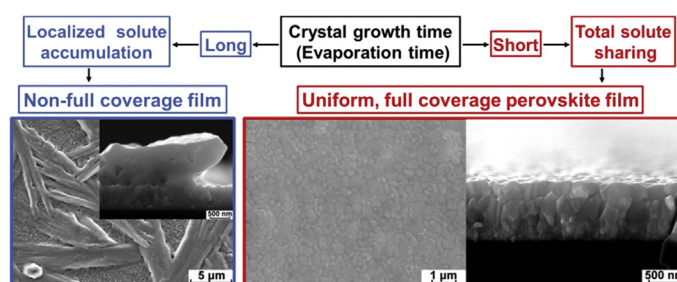
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HIGHLIGHTS

- The general uncovered areas indeed have an ultra-thin layer of $\text{CH}_3\text{NH}_3\text{PbI}_3$ film.
- Long evaporation time results in localized solute accumulation.
- Localized solute accumulation was responsible for the non-full coverage.
- The full coverage film was achieved by decreasing the solvent evaporation time.
- Perovskite solar cells show η of more than 14% with a full coverage film.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 26 January 2016

Received in revised form

18 April 2016

Accepted 20 April 2016

Available online 29 April 2016

Keywords:

$\text{CH}_3\text{NH}_3\text{PbI}_3$ film

Growth behavior

Full coverage

Perovskite solar cells

ABSTRACT

The full coverage of the perovskite film on the substrate surface is of significant importance for the high performance perovskite solar cells. In order to obtain full coverage perovskite films by one-step deposition method, the microstructures of both uncovered areas and covered areas of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film are comparatively investigated. Results show that the uncovered area indeed has an ultra-thin layer of $\text{CH}_3\text{NH}_3\text{PbI}_3$ film which is too thin to cover the rough surface morphology of the substrate, and the localized solute accumulation due to long crystal growth time is responsible for the non-full coverage of the perovskite film. Then by decreasing the crystal growth time, the localized solute accumulation is eliminated gradually and subsequently a full coverage of perovskite film on substrate surface is realized. As a result, the perovskite solar cells show a conversion efficiency of ~13% with the uniform and full coverage perovskite film.

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1. Introduction

Perovskite solar cells are being rapidly developed owing to their

low cost, easy fabrication and high photo-to-electric conversion efficiency [1–4]. Recently, the planar heterojunction configuration perovskite solar cells, which are more suitable for roll-to-roll process, have attracted much attention [5–7]. In order to achieve a high efficiency planar solar cell, the perovskite film must be prepared on the substrate with a full coverage to prevent current leakage on the uncovered region [8–11].

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Until now, one-step deposition method was the most commonly used method to prepare perovskite film due to its low cost and none reverse reaction [12–15]. By using this method, the perovskite films can be simply prepared from precursor solutions containing mixed alkylammonium halides and metal halides by solution film distribution with subsequent natural drying [16–18]. However, the uncontrolled precipitation of perovskite always generates a dendritic structure leaving a lot of uncovered areas on substrate surface [19–21].

Therefore, a couple of methods have been proposed to improve the coverage ratio of the perovskite film by one-step deposition method. Some reports showed that the replacement of inorganic precursor by lead acetate [22] or lead nitrate [23] could improve the film coverage ratio. Besides, adding some additives in the precursor solution, such as hydroiodic acid (HI) [24], 1-chloronaphthalene (CN) [25], poly-(vinylpyrrolidone) (PVP) [26], could also improve the film coverage ratio. However, both types of method need to remove additives, which will bring unpredictable effects to the perovskite film [27,28]. Barrows et al. [29] reported that the coverage ratio was obviously improved with the substrate temperature increased from 28 °C to 75 °C during spray-coating. Jeng et al. [30] found that when the substrate was preheated to 60 °C and the spin-coating speed was improved to 9500 rpm, the number density of void or crevice on the film were markedly reduced. Huang et al. [31] used the 40 psi dry argon gas stream to blow over the film during spin coating, and then a uniform flat $\text{CH}_3\text{NH}_3\text{PbI}_3$ film was formed. According to the above investigations, it was found that the tuning of evaporation, i.e. the decrease of the solvent evaporation time, should be beneficial to the full coverage film. However, to the best of our knowledge the relationship between the solvent evaporation time and the microstructures of the films has not been systematically reported, and the fundamental physics from non-full coverage to full coverage is still unclear.

In this study, after a comparatively investigation on the microstructures of both uncovered areas and covered areas of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ films, the formation mechanism of uncovered surface was discussed. By decreasing the crystal growth time, the morphologies evolution of the perovskite films depending on crystal growth time was investigated. Then the full coverage of perovskite film on substrate surface was realized by eliminating the localized solute accumulation. At last, the uniform and full coverage perovskite film was prepared on ZnO/FTO substrate and assembled into planar configuration solar cells.

2. Experimental

2.1. Solution and film preparation

Lead iodide (PbI_2) and methylammonium (ICH_3NH_3) purchased from Weihua Solar Energy Co. (China) were used as solute. *N,N*-dimethylformamide (DMF) purchased from Sigma-Aldrich (Germany) was used as solvent. All the chemicals were reagent grade and used without further purification. The transparent fluorine-doped tin oxide (FTO, TEC-15, LOF) conductive glasses (25 mm × 25 mm) were employed as substrates. In addition, the indium-doped tin oxide coated polyethylene naphthalate (ITO-PEN, PECF-IP, Peccell) with a similar rough surface as FTO glass and silicon wafer (Si, IC-Dummy, Branch) were all employed as substrates. Before the film deposition, the substrates were cleaned in successive ultrasonic acetone and alcohol bath followed by drying using high purity nitrogen gas.

For precursor solution preparation, PbI_2 and ICH_3NH_3 with stoichiometric amounts were dissolved in DMF solvents with concentration of 35 wt.% and then kept at 70 °C for more than 5 h by using laboratory type magnetic stirrer. Before perovskite film

preparation, the precursor solution was filtered using PTEE filter with a pore size of 0.2 μm . The perovskite film was prepared by the following steps. Firstly, the precursor solution was dropped on the substrate surface and spin-coating at 4000 rpm for 10 s. Secondly, the samples were transferred to a chamber and dried at different low pressures (1800 Pa, 540 Pa, 400 Pa, 170 Pa and 10 Pa). The chamber pressure was controlled automatically by the equipment control unit. All the processes were carried out in air without inert gas protection. During the film preparation the laboratory temperature was kept below 25 °C.

2.2. Device fabrication

A compact layer of ZnO was deposited on the etched FTO substrate (ZnO/FTO substrate) by ion sputtering and then annealed at 120 °C for 15 min. Subsequently, the perovskite film was deposited on the compact ZnO/FTO substrate and dried at the low pressure of 10 Pa. After the as-prepared film was annealed at 100 °C for half an hour, the 2, 2', 7, 7' - tetrakis(*N,N*-di-*p*-methoxyphenylamine) - 9, 9' - spirobifluorene (spiro-OMeTAD) based hole transport layer (HTM) was deposited by spin coating at 3000 rpm for 30 s, where the HTM solution consisted of 80 mg spiro-OMeTAD, 28.5 μL 4-*tert*-butylpyridine and 17.5 μL lithium - bis(trifluoromethanesulfonyl)imide (Li-TFSI) solution (520 mg Li-TFSI in 1 ml acetonitrile), dissolved in 1 ml chlorobenzene. Finally, a 10 nm thick Mo_2O_3 and 200 nm thick Ag layer was deposited on the HTM layer by thermal evaporation respectively.

2.3. Characterization

The surface morphologies of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ films were examined by field emission scanning electron microscopy (FESEM, TESCAN, Czech Republic). The x-ray diffraction (XRD) patterns of perovskite film and substrate were obtained by using an x-ray diffractometer (SHIMADZU, Japan) with $\text{Cu K}\alpha$ radiation. To quantitatively analyze the elements content of the ultra-thin perovskite layer, energy dispersive x-ray spectroscopy (EDS, Oxford, United Kingdom) was employed. The coverage ratio and thickness of the films were calculated with the Image J software (Image J2x, 2011) from the SEM images (at least 10 images for each of data). The photocurrent density-voltage (*J-V*) curves of the solar cells were measured by a solar simulator (84 mW cm^{-2} , Oriol 94023A, Newport) equipped with a Keithley 2400 digital source meter. The exact light intensity was calibrated using a single-crystal silicon photovoltaic cell as the reference (91150V, Oriol Instruments). The cells were measured with a metal mask covered with an area of 0.10 cm^2 to receive sunlight.

3. Results and discussion

3.1. Microstructures of perovskite film prepared by natural drying

Fig. 1a shows the microstructures of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film prepared by one-step solution method with subsequent natural drying. It can be seen that the perovskite crystals tend to gather together showing a dendritic structure, leaving a large area of nano-rough solid surface. The rough areas (as marked by white triangle in Fig. 1a) are widely recognized to be bare FTO based on the SEM results at a relatively low magnification [13,20,25,30,32]. To make clear that if this kind of rough surface is bare substrate surface, the rough areas was exposed to higher magnification observation. Fig. 1b shows the high magnification surface morphology of this kind of rough surface area. Compared with the surface morphology of a bare FTO substrate in Fig. 1c, it can be seen that, under the natural drying condition, the widely reported

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