Morphology Control of MAPbI₃ Perovskite Thin Film as An Active Layer of Solar Cells

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Abstract. With one-step deposition, organic-inorganic perovskite solar cells with planar structure configuration can be produced. This technique has excellent potential for easy fabrication but it results in poor coverage of the film and thus affects the solar cells performance. In this research, morphology control was performed to improve the structure of the MAPbI₃ active layer by flowing hot air during one-step deposition. This allows the fabrication of simple, reproducible MAPbI₃ perovskite thin film with reduced pinhole formation. The hot airflow during the spin coating process homogeneously distributed grains of about 110 nm in size. A power conversion efficiency of 0.91 % was obtained with fill factor of 0.31 under a homemade sun simulator. The results indicate that hot airflow with reduced pinhole formation is a likely choice to control the morphology of thin film perovskite MAPbI₃ for solar cells.

Keywords: perovskite, solar cells, hot airflow, morphology control.

1. Introduction

Organic-inorganic perovskite materials have received much interest for scientific study and device application due to their unique optical, electronic, magnetic properties, and facile film processing [1-3]. Organic-inorganic perovskite materials are currently among the most competitive candidates for absorber materials in thin-film photovoltaic applications. In the past ten years remarkably high efficiencies of ~22% have been reported [4]. The reason for the rapid increase in power conversion efficiency (PCE) of such devices is that perovskite materials have an appropriate direct band gap, high absorption coefficient, and excellent carrier transport [1]. Therefore, one of the main challenges is the fabrication of high-quality films with controlled morphology, high surface coverage and minimum pinhole formation for high performance in perovskite devices.

One of the simplest techniques to fabricate solar cells is one-step deposition using spin coating on both the mesoscopic and planar structure. In previous studies, the planar structure of the perovskite active layer tends to produce higher pinhole density than the mesoscopic structure [5]. This affects low coverage, which causes low absorption in solar cell devices. However, the mesoscopic structure results in a less homogeneous film with the formation of islands during film growth on the TiO₂ [6]. Consequently, areas are uncovered by the perovskite layer [7]. A two-step sequential deposition method has been introduced but it results in a coarse morphology due to particles in the PbI₂ film. This technique is more suitable for solar cells with a mesoscopic structure [8].

A way to improve the reproducibility of perovskite MAPbI₃ is to control the morphological structure by increasing coverage and reducing pinhole formation. Fuzhi Huang reported the first gas-assisted...
preparation of perovskite film in 2014 [13]. Perovskite thin film was grown assisted by gas (argon) during spin coating, obtaining a single crystal monolayer and thus increasing the solar cell efficiency with 16.5%. In 2017, Seulki et al. stated that hot airflow could induce the early steps of MAPbI$_3$·Cl$_x$ crystal growth and yielded a PCE of 14.9% [10].

We have reported the morphological control of perovskite MAPbI$_3$ solar cells with a planar structure under high relative humidity (RH ±70%). The perovskite MAPbI$_3$ material is the optimum perovskite material for use as an active layer of solar cells because it has excellent stability [9]. Morphology control was done by applying hot airflow during the spin coating process. This was expected to improve the process of film growth by accelerating the evaporation process of MAPbI$_3$ solution. Thus, in general, attempts were made to improve the performance of solar cell devices with simple structures and processes.

2. Experiments

2.1 Materials

MAI or CH$_3$NH$_3$I was synthesized by reacting 24 mL of methylamine (33 wt% in ethanol) and 10 mL of hydroiodic acid (57 wt% in air, Sigma Aldrich) and 100 mL ethanol absolute in a three-neck flask under nitrogen at 0 °C for 2 hours with stirring. After the reaction, the white precipitate of CH$_3$NH$_3$I was collected by homemade rotary evaporator at 60 °C. Lead (II) iodide (PbI$_2$) was purchased from Sigma Aldrich. SnO$_2$: Fluorine-doped (FTO), 7 Ohm/sqm, anhydrous N, N-dimethylformamide (DMF), titanium (IV) isopropoxide (TTIP), graphene was purchased from Sigma Aldrich.

2.2 Solar Cell Fabrication

FTO glasses were cleaned in an ultrasonic bath with detergent, de-ionized water, acetone, 2-propanol, and ultrapure water for 5 minutes, respectively. The clean FTO was then dried by nitrogen gun. After being treated, a compact-TiO$_2$ layer was deposited onto the cleaned FTO substrates by spin coating a solution of titanium (I-V) isopropoxide (0.3 ml) in ethanol (5 ml) and hydrochloric acid (0.1 ml) with a speed of 3000 rpm and then sintered at 450 °C for 30 minutes. For the perovskite layer, a 0.88 M perovskite solution was prepared from PbI$_2$ and MAI (1:1-mole ratio) in DMF and spin-coated onto the FTO/TiO$_2$ substrate at 2000 rpm. After 5 s, hot airflow at 100 °C was blown over the surface of the perovskite films during the spin coating process. The flowing rate was varied at 1.5 m/s, 1.7 m/s, and 2 m/s. The distance of the substrate to the hot air nozzle was controlled at 2-3 cm. The perovskite films were then dried at 100 °C for 10 minutes on a hotplate. The final devices were completed by spreading 0.05 g of graphene contacts and putting FTO on top of the graphene contacts. The active area of the devices was 1 cm$^2$.

2.3 Instruments and Characterization

X-ray diffraction (XRD) data were collected on Panalytical X’Pert Pro PW 3040 X-ray Powder Diffractometer. Scanning electron microscopy (SEM) was performed with field-emission electrons using an SEM Hitachi SU3500 instrument. Optical properties were measured with Spectra Suite and an Ocean Optic HR2000CG-UV-NIR instrument. The photovoltaic performance was characterized with an FTO encapsulation sandwich under illumination of a metal halide lamp in a homemade solar simulator, calibrated with silicon solar cell devices. The intensity was calculated using the lux to watts formula.

3. Results and Discussion

Morphology control of thin-film growth was carried out by providing a hot airflow at 100 °C during the process of one-spin coating using an additional heater kit. The effect of hot airflow during spin coating on the initial condition was analysed using an optical microscope with 1000x magnification. Figure 1 shows the initial conditions of the crystallization of MAPbI$_3$. The image was taken using an optical microscope at 10 seconds after the spin-coating deposition process.
Figure 1. Optical microscope images of initial stage of perovskite film crystallization: (a) without hot airflow (b) 1.5 m/s, (c) 1.7 m/s, and (d) 2 m/s of hot airflow rate.

The sample without hot airflow shows irregularly distributed needle-like shapes with low coverage. This is due to the DMF as a solvent not being entirely evaporated so that only a few initial particles were formed (Figure 1a). The sample with hot airflow at a rate of 1.5 m/s indicates uniformly distributed initial particles with high coverage and a lower size of initial particles. The presence of hot airflow during the spin coating caused the solvent to reach supersaturation. The samples with hot airflow at rates of 1.7 m/s and 2 m/s did not adequately show the morphology of the films. We conclude that the initial particle size became smaller and the solvent reached supersaturation faster. DMF has a boiling temperature of 153 °C, so the evaporation process on perovskite film will take a long time. In general, the process of precipitation of a solution onto a film involves two conditions: nucleation and crystal growth. Nucleation will be formed when the solution reaches supersaturation and the initial particles created will depend on the rate of nucleation and the degree of supersaturation. Thus, slow evaporation indicates a low degree of precursor supersaturation. This will cause crystal growth with a small number of particles and with aggregation on the surface as shown in Figure 1a. The flow of hot air during the deposition process is one of the approaches to control the state of precursor supersaturation as shown in Figure 1b. This is consistent with what has been reported in previous studies [10].

Furthermore, the samples were annealed at 100 °C for 10 minutes to finalize the crystal growth and were observed using a scanning electron microscope, as shown in Figure 2. The images show that the formed needle-like shapes indicate the growth of MAPbI₃ film. The films without hot airflow treatment had a large grain size (about 440 nm) and low coverage. The surface of FTO/TiO₂-c was not fully covered by the perovskite layer, which could decrease the device performance because the uncovered part or pinhole area would be a trap for electrons and cause recombination around the interface. Figure 2b shows the sample with hot airflow of 100 °C at a rate of 1.5 m/s resulting in needle-like shapes with a lower grain size. Besides, the resulting films show lower pinhole density.

Figure 2. SEM images of perovskite film (a) without hot airflow (b) 1.5 m/s, (c) 1.7 m/s, (d) 2 m/s of hot airflow rate.

The higher the flow rate given (Figure 2c and 2d), the denser the film surface, the lower the pinhole density and the smaller the crystal grain size, but the higher the coverage. High environmental humidity can cause a small grain size. The growth process of perovskite MAPbI₃ thin film is influenced by environmental humidity [11]. Low humidity can reduce grain boundaries because the grains aggregate more easily. However, the addition of hot airflow during the deposition process at
high humidity leads to speeding up the crystallization process, resulting in a smaller crystal size but higher coverage. Hot airflow induces faster solidification of the film [12].

![Vegetarian Food](https://via.placeholder.com/150)

**Figure 3.** UV-Vis spectra of perovskite thin film.

| Hot airflow rate | Bandgap (eV) |
|------------------|--------------|
| 0 m/s            | 1.44         |
| 1.5 m/s          | 1.51         |
| 1.7 m/s          | 1.52         |
| 2 m/s            | 1.51         |

**Table 1.** Results of Film Band Gaps Obtained from Absorbance Curve of UV-Vis-NIR Spectra

The optical characteristics of the perovskite MAPbI$_3$ films were obtained by using UV-Vis spectrophotometric measurement. Figure 3 shows the absorbance curve and wavelength for each sample. It can be seen that the presence of hot airflow improved the absorbance of the perovskite films with absorbance onset at a wavelength of 750 nm, consistent with the report from Huang et al. [13]. The higher the hot airflow rate, the higher the film’s ability to absorb light. This is related to the film morphology. The presence of hot airflow can improve film density as a function of the surface. Also, the band gap can be calculated from this curve, as shown in Table 1. Based on the Tauc-plot equation, bandgap calculations of 1.51 eV and 1.52 eV from the hot airflow treatment were obtained, while 1.44 eV was obtained from the film without hot airflow treatment. The presence of hot airflow caused a blue shift in the absorbance curve. As a consequence, there was a band gap difference between the samples. This is different from conventional semiconductor theory. The higher the temperature, the lower the resulting band gap. This is because of the occurrence of smaller valence band shifts due to the effect of temperature on MAPbI$_3$ films [14].
XRD characterization of the films with a flow rate of 2 m/s (Figure 4) was conducted. Peaks at an angle of 2θ were obtained, corresponding to the reference, where the dominant peaks are (1 1 0), (2 2 0), and (3 1 0), respectively, at angles of 14.04°, 26.43°, and 31.81°. Based on the XRD results, it was found that the MAPbI$_3$ thin film had a tetragonal crystal structure [15].

The optimum film morphology was obtained from a flow rate of 2 m/s. The I-V characteristics of the device fabricated were shown in Figure 5. The low value of PCE produced by the device could be caused by the recombination of electron-hole pairs before they reached the electrode. Furthermore, graphene powder as an electrode grown by spreading produces a less even layer, which could lead to electron traps.

4. Conclusions
In summary, hot airflow during spin coating deposition was developed to fabricate higher coverage of perovskite thin films as an active layer in solar cells devices under high humidity. This method facilitates faster evaporation of the solvent by increasing a degree of supersaturation. Consequently, more evenly distributed particles with low grain size were obtained and the morphology and optical characteristics of the film were improved.
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