Effect of Air-Flow and Solvent Annealing on Fabrication of Perovskite Active Layer and Photovoltaic Properties of Cells with the Active Layer

Tatsuo Mori*, Hiroyuki Okada, Vincent Obiozo Eze, and Yoshiyuki Seike

Department of Electrical and Electronic Engineering, Graduate School of Engineering, Aichi Institute of Technology, 1247 Yachigusa, Yakusa-cho, Toyota, Aichi 470-0392, Japan
*t2mori@ai-tech.ac.jp

In perovskite solar cells, the morphology of perovskite active layers is one of important factors for obtaining high energy conversion efficiency (PCE). We investigate the morphology of the crystals and grains of perovskite layer fabricated by a 1-step method incorporated with the air-flow and solvent annealing. Although the crystal and grain sizes of perovskite layer became smaller than the as-grown perovskite layer, the former film quality advanced because of less pinhole. In addition, after the solvent annealing, the crystals and grains of perovskite layer grew promptly in the air-flow treated perovskite layer. The crystal and grain sizes in the air-flow treated perovskite layer were twice larger than those in the as-grown perovskite layer. Finally we fabricated the higher PCE perovskite solar cells by incorporating the air-flow and solvent annealing processes.

Keyword: Perovskite solar cell, Air-flow, Solvent annealing, Crystal morphology, Crystal Growth

1. Introduction

In the study of perovskite solar cells, 10 years have passed since the first Miyasaka group’s report in 2009 [1]. Now the power conversion efficiency (PCE) of perovskite solar cells exceeded 25% in 2019 [2]. As is well-known, the device performance depends on humidity as well as fabrication process [3]. Perovskite solar cells have the structure of the light-absorbance (perovskite) layer sandwiched by hole and electron extraction layers. Therefore, it is desirable that perovskite crystals directly contact with both carrier extraction layers through grain boundaries and interfaces. Of course, larger crystals and grains are preferred.

Post-treatments for the encouragement of crystal growth are important. Two post-treatments are well-known for the improvement of the morphology of perovskite layer. One is the solvent engineering (another name, anti-solvent) method and the other is the solvent annealing method. The solvent engineering method was reported by Seok group [4]. In the solvent engineering method, such poor solvent as a toluene is dropped on the perovskite layer soon after spin-coating and a gentle crystal growth are encouraged. On the other hand, the solvent annealing method was reported by Cheng group [5]. In the solvent annealing, the perovskite layers are kept in the saturated vapor atmosphere of such a solvent as dimethylsulfoxide (DMSO) or dimethylformamide (DMF) at ~423K. After the previously formed perovskite crystals are dissolved by solvent molecules, the perovskite crystals grow larger with reconstituting.

The main fabrication process of perovskite layers are categorized by solution and vacuum deposition methods [6]. Although comparatively uniform and high quality perovskite layer can be fabricated by the vacuum deposition method, the expensive manufacture cost is an inevitable problem. On the other hand, there are 1-step and 2-step methods in the solution method. In the 1-step method, the perovskite layer is fabricated by casting the mixture solution including all material sources. In the 2-step method, the perovskite layer is converted by a post immersing treatment after
forming precursors. Now it is reported that many high-performance perovskite solar cells have been fabricated by the 1-step method [7-9].

Some pinholes often occur during the fabrication process of perovskite layers. The occurrence of these pinholes contributes to the deterioration of device performance. Even if crystal and grain are large, some pinholes will be easily generated by the encounter of adjacent crystals/regions. In addition, it is possible that electrical weak points are generated in the grain boundary. In organic light-emitting diodes, it is well-known that the use of amorphous materials contributes to the commercial viability in order to prevent the degradation of electrical insulation for polycrystalline materials, which have many electrical weak points [10,11].

The gas flow method which perovskite layers are blown by an inert gas during the fabrication was reported by Huang et al. in 2014 [12]. They reported that the film morphology of perovskite layer and PCE of photovoltaic (PV) cells are improved by blowing Ar gas in a glove box. We carried out the air-flow to the 2-step fabrication in order to fabricate PV cells in an air atmosphere in 2015 [13,14]. Gotanda et al. reported that the contact of the perovskite layer with the underlayer is enhanced by the gas-flow during the formation of perovskite layers in inverse structure devices [15]. Although this gas-flow was carried out in a glove box, they reported that the device performance is influenced by not only direct gas-flow but also indirect gas-flow in the glove box strangely [16]. This suggests that even the weak gas-flux in the closed space has a slight impact on the morphology of perovskite layer.

In this paper, we verify the effect of air-flow to the morphology of perovskite layer in order to manufacture PV cells in the air atmosphere. Although it is dangerous to flow such an inert gas as Ar or N2 in a closed space, the use of dry air can avoid the danger. The saturated water vapor amounts at 293 K and at 233 K (the dew-point temperature in air cylinder) are 17.3 and 0.17 g/m³, respectively. The latter is almost hundredth part of the former. We investigate the morphology, crystal condition, etc. of the air-flow treated perovskite layers combined with the solvent annealing and their PV properties. In the air-flow process, it is difficult to apply the solvent engineering because of the inconsistency of both physical concepts, drying and dissolving. Therefore, we incorporate the air-flow process with the solvent annealing in the fabrication process of perovskite layers.

2. Experimental

2.1. Materials and fabrication

Fluorine-doped tin oxides (FTOs) were cleaned by water, organic solvents and tetramethyl ammonium hydroxide in water. TiO2, which was fabricated by the pyrolysis of titanium disopropoxide bis(acetylacetonate) on FTO electrodes, was used as an electron extraction layer. We fabricated perovskite solar cells by a 1-step method in this paper. In the 1-step method, the mixture solution including PbI2 and CH3NH3I (MAI) in γ-butylrolactone and 1-methyl-2-pyrrolidinane was spin-coated on TiO2-deposited FTO. The spin-coating condition without the air-flow process was 3600 rpm, 30 s. In order to uniform the thickness of perovskite film, the spin-coating condition with the air-flow was 4000 rpm, 30 s. The air-flow was carried out using the air-gun (AS-ONE, φ = 3 mm). The air-gun nozzle was located on 10 cm-top of substrate in Fig. 1. The typical air pressure was 0.05 MPa. The air-flow was started after 8 s from beginning of spin-coating. Perovskite films on a 423 K-hotplate were kept in the saturated dimethyl sulfoxide vapor atmosphere for 10 min through dipping in diethyl ether for 90 s (solvent annealing). Spiro-MeOTAD was fabricated as a hole extraction layer by the spin-coating. Au was evaporated as a top electrode. Our devices were a conventional and planar structure consisting of FTO/TiO2/perovskite/spiro-MeOTAD/Au. All experimental procedures were carried out in air atmosphere except for the vacuum deposition of Au electrode.

![Fig. 1. The configuration of the air gun to substrates during the air-flow treatment.](image-url)
observed by field-emission scanning electron microscopy (FE-SEM; JEOL, JSM-6335FM, acceleration voltage of 10 kV). Atomic force microscopy (AFM) images were obtained using Seiko Instruments SPA 400-SPI 4000. Ultraviolet-visible (UV-vis) absorption spectra were measured using a UV-vis spectrophotometer (Shimadzu UV 2450). X-ray diffraction (XRD) patterns were recorded in the 2θ range of 5–60° using an X-ray diffractometer (Rigaku RINT2500V/PC) with Cu Kα radiation (40 kV, 100 mA.). We used a thickness tester (Kosaka Laboratory, Surfcoorder ET200). Current-voltage (J-V) characteristics were measured with a digital source meter (Agilent B2901A). A 150 W xenon lamp (Bunkoukeiki, Otento-SUN3 Xe-S150) was used as the solar simulator of the AM 1.5 G condition (100 mW/cm²).

3. Results and Discussion

3.1. Characteristics of perovskite layers

Figure 2 shows the absorption spectra of the as-grown and air-flow treated perovskite layers (with layer thickness) after the solvent annealing.

Since the air-flow process influences the drying process of perovskite layer, we changed the gas pressure and starting time of air-flow during the spin-coating. The gas pressure changed from 0.05 MPa to 0.025 MPa and the starting time changed from 8 s to 10 s. The gas pressure cannot be increased up >0.05 MPa. When the gas pressure is too high, the surface of perovskite layer is dented by the gas blow. In addition, the air bubbles, which are incorporated during dropping the solution on the substrate, often burst by the strong air-blow before diminishing. Consequently some pinholes of the perovskite layer occur. It is important to optimize the appropriate air-flow treatment condition.

Figures 4(a) and (b) show (a) the AFM images and (b) grain distributions of the air-flow treated perovskite layers after the solvent annealing. The grain morphology was found not to depend on air-flow condition. The average grain size was estimated to be 500-600 nm except for the air-flow treated perovskite layer of 0.025 MPa and 8 s. The grain sizes of the air-flow treated perovskite layer
are smaller than those of the as-grown perovskite. While the average grain size is ~300 nm in the as-grown perovskite layer, that is ~550 nm in the air-flow treated perovskite layer. Since the grain sizes in the air-flow treated perovskite layer are almost twice larger than the thicknesses of perovskite layer, these grains are thought to be bridged between the hole and electron extraction layers.

Fig. 4. (a) The AFM images of the air-flow treated perovskite layers fabricated by various air-flow conditions after the solvent annealing: (b) the distributions of the grain size for the above perovskite layers with the distribution of the grain size for as-grown perovskite layer after the solvent-annealing.

Figures 5(a) and 5(b) show the XRD patterns of

Table 1. The crystallite sizes of 4 specimens.

| specimen   | crystallite size [nm] |
|------------|-----------------------|
| before SA  | AF                    |
|            | as-grown              |
| 19.5       | 23.2                  |
| after SA   | AF                    |
|            | as-grown              |
| 42.9       | 40.8                  |

The crystallite size of CH$_3$NH$_3$PbI$_3$, $D$ can be estimated from the full width at half maximum (FWHM) of the XRD peak using the following
where \( \lambda \) [nm] is the wavelength of Cu K\( \alpha \), \( \beta \) [rad] is the FWHM of the XRD peak \( 2\theta (14.12^\circ = 0.2464 \text{ [rad]}), \theta \) is the diffraction angle, \( 2\theta (14.12^\circ) \), and \( K \) is the Scherrer constant, 0.94 (a typical and well-used value).

We summarize the crystallite size of 4 specimens in Table 1. The grain size of the perovskite layer after the solvent-annealing becomes larger than that before the solvent-annealing. At the same time, the crystallite of the perovskite crystal after the solvent-annealing grows larger than that before the solvent-annealing. Although the crystallite size of the air-flow treated perovskite layer is smaller than that of the as-grown perovskite layer before the solvent-annealing, the former is larger than the latter after the solvent-annealing. Since the grains of >1,000 nm-size exist, the crystallite size is at most \(~40 \text{ nm, which is less than 1/25 of the large grain size.}\)

### 3.2. PV properties of the PV cell with the air-flow treated after the solvent annealing

![Figure 6. The photocurrent curves of the PV cells with the as-grown and air-flow treated perovskite layers.](image)

**Table 2. The summary of PV parameters in Fig. 6.**

| specimen  | \( J_{SC} \) [mA/cm\(^2\)] | \( V_{OC} \) [V] | FF  | PCE [%] |
|----------|-----------------|----------------|-----|--------|
| AF       | 22.0            | 1.07           | 0.664 | 15.7   |
| As-grown | 21.5            | 1.04           | 0.641 | 14.3   |

Figure 6 shows the photocurrent curves of the

PV cells with the as-grown and air-flow treated perovskite layers. The PV parameters of Fig. 6 are summarized in Table 2. The PV performance of the PV cell with the air-flow treated perovskite layer is advanced as compared with that of the PV cell with the as-grown perovskite layer. Since both thicknesses of perovskite layers are almost same, both the short-circuit currents are also same. Both open voltages are also beyond 1 V. However, both fill factors are < 0.7 and poor. The FF must be improved for a high PCE. Unfortunately there is no a profound difference between both the best PV cells. Perhaps the film morphology of the perovskite layer is mainly improved by the effect of the solvent-annealing.

### 4. Conclusion

We investigated the synergistic effect of the air-flow and solvent annealing on the crystal and grain of the perovskite layer fabricated by the 1-step method. The air-flow treatment was effective in homogenizing finer perovskite crystals and grains. Although the air-flow treated perovskite layer had finer perovskite crystals and grains, the crystals and grains of the air-flow treated perovskite layer grew larger during the solvent annealing. The combination process of the air-flow treatment and solvent-annealing was very effective for the improvement of the morphology of perovskite layer and the PV performance.

### Acknowledgements

This research is partially obtained by the AIT Special Grant “Development of Hybrid-Power Science & Technology for Green-Energy”, the AIT special grant for Education and Research, and JSPS Grant-in-Aid for Scientific Research (B) 16H03890 and (C) 17K06171.

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