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# Effects of hot airflow during spin-coating process on CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub> perovskite solar cells

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**Abstract.**  $CH_3NH_3PbI_{3-x}Cl_x$  photovoltaic devices were fabricated, and the effects of hot airflow during spin-coating were investigated. Cubic perovskite crystals that is a high temperature phase were obtained by the hot airflow method. The conversion efficiencies of the devices prepared by the hot airflow were remained even after 56 days.

#### **INTRODUCTION**

Perovskite-type solar cells have attracted much attention, because of their high conversion efficiencies and easy fabrication process [1-4]. However, the structural stability of the perovskite crystal is slightly low at a room temperature, because the cubic-tetragonal phase transition temperature is 330 K [5]. In order to stabilize the cubic perovskite crystal structure, the device temperature should be raised during spin-coating. The hot airflow method during the spin-coating would be one of the way to solve this problem.

The purpose of the present work is to fabricate perovskite  $CH_3NH_3PbI_{3-x}Cl_x$  solar cells by the hot airflow method during spin-coating, and to investigate photovoltaic properties including long-term durability and microstructures by light-induced current density voltage (*J-V*) curves, X-ray diffraction (XRD), and scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDX).

#### **EXPERIMENTAL PROCEDURES**

A schematic illustration of the fabrication process of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub> photovoltaic cells is shown in Fig. 1. The detailed fabrication process was described in the previous reports [6-11]. All process was carried out under ordinary air. F-doped tin oxide (FTO) substrates were cleaned using an ultrasonic bath with acetone and ethanol, and dried under nitrogen gas. Then, FTO substrates were treated with ultra-violet-ozone cleaner (Asumi Giken, ASM401N) for 15 min. TiO<sub>x</sub> precursor solutions of 0.15 M and 0.30 M were prepared from titanium diisopropoxide bis (acetyl acetonate) (Sigma Aldrich) with 1-butanol (Wako Pure Chemical Industries). The 0.15 M TiO<sub>x</sub> precursor solution was spin-coated on the FTO substrate at 3000 rpm for 30 s using a spin coater (Mikasa, MS-A100) and annealed at 125 °C for 5 min. Then, the 0.30 M TiO<sub>x</sub> precursor solution was spin-coated on the TiO<sub>x</sub> layer at 3000 rpm for 30 s and annealed at 125 °C for 5 min. This process using 0.30 M precursor solutions was performed twice. After that, the FTO substrate was sintered at 500 °C for 30 min to form a compact TiO<sub>2</sub> layer. A mesoporous  $TiO_2$  layer was formed by spin-coating at 5000 rpm for 30 s on the compact  $TiO_2$  using  $TiO_2$ paste. TiO<sub>2</sub> paste was prepared with TiO<sub>2</sub> powder (Aerosil, P-25) with poly (ethylene glycol) (Nacalai tesque, PEG #20000) in distilled water [12]. This solution was mixed with acetylacetone (Wako Pure Chemical Industries) and triton X-100 surfactant (Sigma Aldrich) for 30 min, and was left for 12 h to suppress the bubble in the solution. The cells were annealed at 120 °C for 5 min and at 500 °C for 30 min to form the mesoporous TiO<sub>2</sub> layer [13]. For the preparation of the perovskite compounds, mixed solutions of CH<sub>3</sub>NH<sub>3</sub>I (Showa Chemical), PbCl<sub>2</sub> (Sigma Aldrich) in N,N-dimethylformamide (DMF, Sigma-Aldrich) were prepared at 60 °C. Molar concentrations of CH<sub>3</sub>NH<sub>3</sub>I and PbCl<sub>2</sub> were 2.4 M and 0.8 M, respectively. Solutions of the perovskite precursors were spin-coated on the mesoporous TiO<sub>2</sub> at 2000 rpm for 60 s [14-16]. The conditions of air flow and spin-coating are summarized in Table 1. The temperature of the cells during hot airflow were at 90 °C, which were measured by a radiation

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thermometer (Shinwa Rules, 73036). Then, the cells were annealed at 140 °C for 10 min. Next, a hole transport layer (HTL) was prepared by spin-coating. As a HTL, a solution of 2,2',7,7'-tetrakis-[N,N-di(pmethoxyphenyl)amino]-9'9'-spirobifluorene (spiro-OMeTAD, Sigma Aldrich, 36.1 mg) in chlorobenzene (Wako Pure Chemical Industries, 0.5 mL) was mixed with a solution of lithium bis (trifluoromethylsulfonyl) imide (Tokyo Chemical Industry, 260 mg) in acetonitrile (Nacalai tesque, 0.5 mL) for 24 h. The former solution with 4tert-butylpyridine (Sigma Aldrich, 14.4  $\mu$ L) was mixed with the Li-TFSI solution (8.8  $\mu$ L) for 30 min at 70 °C, and cooled to room temperature. Finally, gold (Au) electrodes were evaporated as top electrodes.

The J-V characteristics (Keysight, B2901A) of the photovoltaic cells were measured under illumination at 100 mW cm<sup>-2</sup> by using an AM 1.5 solar simulator (San-ei Electric XES-301S). The solar cells were illuminated through the side of the FTO substrates, and the measurement area was 0.090 cm<sup>2</sup>. The microstructures of the perovskite layers were measured by an X-ray diffractometer (Bruker, D2 PHASER). Lattice constants of the perovskite structures were calculated by a least-square method [17] using *d* values of 100, 200, 210, 220 and 221 diffraction peaks. An optical microscope (Nikon, Eclipse E600) and a scanning electron microscope equipped with an EDX detector (Jeol, JSM-6010PLUS/LA) were also used for the structure analysis.



FIGURE 1. Schematic illustration of fabrication process of the present perovskite solar cells.

**TABLE 1.** Conditions of spin-coating and hot airflow.

Devices	Conditions			
	Spin coating without airflow (times)	Spin-coating with airflow (times)		
Airflow 0	2	0		
Airflow 1	1	1		
Airflow 2	1	2		
Airflow 3	1	3		

#### **RESULTS AND DISCUSSION**

*J-V* characteristics (reverse sweep) of the present photovoltaic cells are shown in Fig. 2, and changes of the photovoltaic properties of the present devices are shown in Table 2 and Fig. 3. The values of the open-circuit voltage ( $V_{OC}$ ) of hot airflow cells were similar to that of non-airflow one.  $V_{OC}$  values of all cells showed similar

values as time proceeded, and the  $V_{OC}$  values of all cells increased even after 56 days. The short-circuit current densities ( $J_{SC}$ ) of the hot airflow cells were higher than that of the airflow 0 cell, which resulted in higher conversion efficiencies. After 28 days, the  $J_{SC}$  values and fill factors (*FF*) of the hot airflow cells increased significantly compared with those of non-airflow one, which resulted in the improvements of the conversion efficiencies. The  $J_{SC}$  values of hot airflow cells slightly decreased after 56 days, and that of airflow 0 cell slightly increased. After 56 days, the airflow 1 cell showed the highest efficiency of 7.29 %.



FIGURE 2. J-V characteristice of the present solar cells (a) after 28 days and (b) after 56 days.

Time (day)	0	3	7	28	56			
Airflow 0								
Jsc (mA cm <sup>-2</sup> )	6.68	8.65	7.33	8.95	10.2			
Voc(V)	0.793	0.719	0.699	0.666	0.748			
FF	0.379	0.473	0.405	0.488	0.361			
η (%)	2.01	2.94	2.07	2.91	2.77			
Airflow 1								
$J_{SC}$ (mA cm <sup>-2</sup> )	9.79	12.8	14.1	14.1	16.0			
Voc(V)	0.897	0.850	0.821	0.735	0.776			
FF	0.520	0.617	0.649	0.593	0.585			
η (%)	4.56	6.70	7.52	6.16	7.29			
	Airflow 2							
$J_{SC}$ (mA cm <sup>-2</sup> )	12.4	10.2	16.9	19.3	17.2			
$V_{OC}(V)$	0.784	0.820	0.774	0.697	0.724			
FF	0.248	0.379	0.509	0.548	0.453			
η (%)	2.42	3.18	6.69	7.38	5.63			
Airflow 3								
$J_{SC}$ (mA cm <sup>-2</sup> )	9.10	4.97	11.5	16.3	16.6			
Voc(V)	0.844	0.875	0.835	0.788	0.791			
FF	0.265	0.252	0.442	0.504	0.472			
η (%)	2.03	1.10	4.25	6.49	6.19			

TABLE 2. Changes of the photovoltaic characteristics of the present solar cells.

XRD patterns of the as-prepared perovskite cells are shown in Fig. 4. For the hot airflow cells, highly 100 oriented peaks of cubic perovskite structure are observed. The cell temperature during the hot airflow was 90 °C (363 K), which is higher than the cubic-tetragonal transition temperature of 330 K. Therefore, the cubic perovskite would be formed during the hot airflow and might be frozen as the cubic structure. Calculated lattice constants of the as-prepared perovskite crystals of the present cells are shown in Fig. 5. As the times of airflow increased, the lattice constants decreased, which might be desorption of  $CH_3NH_3$  during the crystallization by the hot airflow.



**FIGURE 3.** Changes of the (a)  $J_{SC}$ , (b)  $V_{OC}$ , (c) FF, and (d)  $\eta$  of the present solar cells

Optical microscope images of the present cells are shown in Fig. 6. For the cell of airflow 0, the spherical particles with sizes of  $\sim 20 \ \mu\text{m}$  were observed, as shown in Fig. 6(a). The particle sizes of the airflow 0 cells decreased drastically by the hot air flow, as observed in Fig. 6(b)-6(d). For the airflow 2 and 3 cells of Fig. 6(c) and 6(d), particles with angular facets are observed, which would derive from the cubic structure. The surface coverages of the perovskite layers for the hot airflow cells were improved compared with that of airflow 0 cell, leading to the improvement of the photovoltaic properties.

SEM images of the present cells are shown in Fig. 7. For the airflow 0 cell, flower-like particles with sizes of  $20 \sim 30 \ \mu\text{m}$  are observed, as shown in Fig. 7(a). The particle sizes decreased to  $5 \sim 10 \ \mu\text{m}$  by the hot airflow 1, as observed in Fig. 7(b). For the cells prepared by the airflow 2 and 3, the particles with flat surfaces are observed, as shown in Fig. 7(c) and 7(d), respectively. These flat facets are considered to be (100) planes of cubic CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, which was also confirmed by the strong 100 peaks in Fig. 4(c) and 4(d).



FIGURE 4. XRD patterns of (a) airflow 0, (b) airflow 1, (c) airflow 2, and (d) airflow 3 cells.



FIGURE 5. Measured lattice constants of the present perovskite crystals from XRD patterns.



FIGURE 6. Optical microscope images of (a) airflow 0, (b) airflow 1, (c) airflow 2, and (d) airflow 3 cells.



FIGURE 7. SEM images of (a) airflow 0, (b) airflow 1, (c) airflow 2, and (d) airflow 3 cells.

#### CONCLUSIONS

 $CH_3NH_3PbI_{3-x}Cl_x$  perovskite solar cells were fabricated by changing the times of hot airflow during the spincoating, and the effects of the hot airflow of the  $CH_3NH_3PbI_{3-x}Cl_x$  perovskite solar cells on the photovoltaic properties and microstructures were investigated. The conversion efficiencies of hot airflow cells were higher than that of non-airflow cell, and the efficiencies of airflow cells were improved after 28 and 56 days. Highly (100)oriented cubic perovskite particles were formed by the hot airflow. The temperature of the hot airflow was higher than the cubic-tetragonal transition temperature of the  $CH_3NH_3PbI_3$ .

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