Highly (100)-oriented CH$_3$NH$_3$Pbl$_3$(Cl) perovskite solar cells prepared with NH$_4$Cl using an air blow method\textsuperscript{†}

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The effects of adding NH$_4$Cl via an air blow process on CH$_3$NH$_3$Pbl$_3$(Cl) perovskite solar cells were investigated. CH$_3$NH$_3$Pbl$_3$(Cl) solar cells containing various amounts of NH$_4$Cl were fabricated by spin-coating. The microstructures of the resulting cells were investigated by X-ray diffraction, optical microscopy, and scanning electron microscopy. The current density–voltage characteristics of the cell were improved by adding an appropriate amount of NH$_4$Cl and air blowing, which increased the photoconversion efficiency to 14%. Microstructure analysis indicated that the perovskite layer contained dense grains with strong (100) orientation, as a result of NH$_4$Cl addition and air blowing. The ratio of the (100)/(210) reflection intensities for the perovskite crystals was 2000 times higher than that of randomly oriented grains. The devices were stable when stored in ambient air for two weeks.

Introduction

Thin film solar cells containing methylammonium trihalogenomplumbate(n) (CH$_3$NH$_3$PbI$_3$) compounds with perovskite structures have recently been widely studied.\textsuperscript{1–4} This has been due to their easy fabrication processes and high photovoltaic efficiencies compared with conventional fullerene-based organic solar cells. Conversion efficiencies for these conventional cells have reached 15%,\textsuperscript{5} but higher efficiencies have been achieved for various perovskite compounds and device structures.\textsuperscript{6–8} Conversion efficiencies above 20% have been reported.\textsuperscript{9–18}

The photovoltaic properties of perovskite-based solar cells depend on the composition and crystal structure of the perovskite compound. Introducing metal atoms such as tin (Sn),\textsuperscript{19,20} antimony (Sb),\textsuperscript{21–25} copper (Cu),\textsuperscript{26} arsenic (As),\textsuperscript{27} germanium (Ge),\textsuperscript{28,29} indium (In),\textsuperscript{29} or thallium (Tl)\textsuperscript{29} at lead (Pb) sites has been performed. The optical absorption range of perovskite compounds has been extended by Sn or Tl doping.\textsuperscript{19,20,29}

Introducing cesium,\textsuperscript{18} rubidium,\textsuperscript{14} formamidinium (NH=CHNH$_3$, FA)\textsuperscript{30} or ethylammonium (CH$_3$CH$_2$NH$_3$, EA)\textsuperscript{31} at methylammonium (CH$_3$NH$_3$, MA) sites can also improve conversion efficiencies. Studies on doping with bromine (Br),\textsuperscript{32,33} or chlorine (Cl)\textsuperscript{34,35} at iodine (I) sites of perovskite crystals have been reported. Doping with Cl reportedly increases the diffusion length, which improves the conversion efficiency.\textsuperscript{31,32} Various elemental and molecular dopants at Pb, I, and/or MA sites reportedly affect the photovoltaic properties and microstructures of perovskite-based solar cells.\textsuperscript{44}

Photovoltaic properties also strongly depend on the morphology of thin films.\textsuperscript{35} A large interfacial area between the perovskite layers and TiO$_2$ electron transport layers can increase carrier separation, which increases the short circuit current density. Smooth and homogeneous surfaces, interfaces, and grain boundary structures of perovskite layers are expected to result in improved open circuit voltages and fill factors.\textsuperscript{36}

The present study investigates the effects of adding NH$_4$Cl to perovskite CH$_3$NH$_3$PbI$_3$(Cl) photovoltaic devices, using a hot air blow method. NH$_4$Cl has surfactant properties, so is expected to promote a homogeneous morphology.\textsuperscript{37–39} The doped Cl is expected to increase the carrier diffusion length in the perovskite crystals.\textsuperscript{53} The Cl-doped perovskite crystals are denoted as CH$_3$NH$_3$PbI$_3$(Cl) in the present study. The effects of NH$_4$Cl addition on the formation of perovskite compounds for photovoltaic cells are investigated by light-induced current density–voltage (J–V) measurements, incident photon-to-current conversion efficiency (IPCE), X-ray diffraction (XRD), optical microscopy (OM), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS).

Experimental

Materials

All reagents and solvents were used as received. For the compact TiO$_2$ layer, 0.15 M and 0.30 M TiO$_2$ precursor solutions were prepared from titanium diisopropoxide bis(acetylacetone) (Sigma-Aldrich, 0.055 mL and 0.11 mL, respectively) with 1-butanol (1 mL). For the mesoporous TiO$_2$ layer, TiO$_2$ paste was prepared using TiO$_2$ powder (Nippon Aerosil, P-25) with...
poly(ethylene glycol) (Nacalai Tesque, PEG #20000) in ultrapure water. The resulting dispersion was mixed with acetylacetone (Wako Pure Chemical Industries, 10 μL) and Triton X-100 (Sigma-Aldrich, 5 μL), stirred for 30 min, and then left to stand for 12 h to allow bubbles in the mixture to disperse.

For the perovskite layer, a solution containing CH₃NH₃I (Showa Chemical Co., Ltd., 190.7 mg) and PbCl₂ (Sigma-Aldrich, 111.2 mg) was prepared with a molar ratio of 3 : 1 in N,N-dimethylformamide (Nacalai Tesque, 0.5 mL). This solution was then stirred at 60 °C for 24 h.

For the hole transport layer, two solutions of 2,2',7,7'-tetrakis[N,N-di(p-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD, Sigma-Aldrich, 36.1 mg) in chlorobenzene (Wako Pure Chemical Industries, 0.5 mL) and lithium bis(trifluoromethylsulfonyl)imide (Li-TFSI, Tokyo Chemical Industry, 8.8 mg) in acetonitrile (Nacalai Tesque, 0.5 mL) were prepared and stirred for 12 h. The former spiro-OMeTAD solution in chlorobenzene containing 4-tert-butylpyridine (Aldrich, 14.4 μL) was mixed with the latter Li-TFSI solution (8.8 μL), and the resulting solution was stirred for 30 min at 70 °C.

Device fabrication

Fig. 1 shows a schematic illustration of the process used to fabricate the TiO₂/CH₃NH₃PbI₃(Cl) photovoltaic cells. Details of the basic fabrication process have been described previously, with the exception of details of the air blow procedure. F-doped tin oxide (FTO) substrates were ultrasonically cleaned with acetone and methanol, and then dried under nitrogen gas. The 0.15 M TiO₂ precursor solution was spin-coated onto the FTO substrate at 3000 rpm for 30 s, and the coated substrate was then heated to 125 °C for 5 min in air to form a TiO₂ layer.

The 0.30 M TiO₂ precursor solution was spin-coated onto the TiO₂ layer at 3000 rpm for 30 s, and the coated substrate was then heated at 125 °C for 5 min. This process of coating with 0.30 M solution was performed a second time, and the resulting FTO substrate was then annealed at 500 °C for 30 min to form a compact TiO₂ layer. For the mesoporous TiO₂ layer, the TiO₂ paste was spin-coated onto the substrate at 5000 rpm for 30 s. The substrate was then annealed at 120 °C for 5 min, and then at 500 °C for 30 min, to form a mesoporous TiO₂ layer.

Then, a solution containing CH₃NH₃PbI₃(Cl) was introduced into the TiO₂ mesopores of the above coated substrate by the spin-coating method. For the spin-coating procedure, air blowing at a rate of 6 m s⁻¹ and 3300 cm³ s⁻¹ was applied perpendicular to the substrate at a temperature of 90 °C for 60 s, as indicated in Fig. 1. The resulting substrate was annealed at 140 °C for 10 min to form the perovskite layer.

A hole transport layer was then prepared by spin-coating onto the perovskite layer. All procedures for preparing thin films were performed in ambient air at a temperature of 28 °C and humidity of ~50%. Finally, a gold (Au) thin film was evaporated onto the hole transport layer, as the top metal electrode. The layered structure of the solar cell was denoted as FTO/TiO₂/CH₃NH₃PbI₃(Cl)/spiro-OMeTAD/Au, as shown in Fig. 1.

Characterization

The J–V characteristics of the photovoltaic cells were measured under illumination at 100 mW cm⁻², using an AM 1.5 solar simulator (San-ei Electric, XES-301S). J–V measurements were performed using a source measure unit (Keysight, B2901A Precision SMU). The scan rate and sampling time were ~0.05 V s⁻¹ and 1 m s, respectively. Four cells were tested for each cell composition. The solar cells were illuminated through the sides of the FTO substrates, and the illuminated area was 0.090 cm². IPCE of the cells were also measured (Enli Technology, QE-R). The microstructures of the cells were investigated using an X-ray diffractometer (Bruker, D2 PHASER), a transmission optical microscope (Nikon, Eclipse E600), and a scanning electron microscope (Jeol, JSM-6010PLUS/LA) equipped with EDS.

Results and discussion

Fig. 2 shows the J–V characteristics of the TiO₂/CH₃NH₃PbI₃(Cl)/spiro-OMeTAD photovoltaic cells under illumination, in which the effects of NH₄Cl addition are evident. Forward and reverse scans are indicated by the dotted and solid lines, respectively. The measured photovoltaic parameters of the TiO₂/CH₃NH₃PbI₃(Cl) cells are summarized in Table 1, and forward (Fw) and reverse (Rv) values are listed. Small hysteresis between the forward and reverse scans is observed for the J–V characteristics in Fig. 2, and the degree of hysteresis decreases with NH₄Cl addition. A small amount of carriers may have been generated.
Fig. 2  J–V characteristics of CH$_3$NH$_3$PbI$_3$(Cl) solar cells with and without NH$_4$Cl.

and transported into the TiO$_2$ layer during the J–V measurements (i.e. during light irradiation and subsequent current flow). In this case, the electrical resistance would decrease and the photocurrent would increase, resulting in the hysteresis. The perovskite would also exhibit hysteresis properties in its J–V characteristics. The perovskite would also exhibit hysteresis properties in its J–V characteristics.

The CH$_3$NH$_3$PbI$_3$(Cl) cell without NH$_4$Cl provides a power conversion efficiency ($\eta$) of 12.41% for the reverse scan. The highest efficiency CH$_3$NH$_3$PbI$_3$(Cl) cell, with a FF of 0.685, J$_{SC}$ of 22.6 mA cm$^{-2}$, and $V_{OC}$ of 0.908 V. The highest average power conversion efficiency ($\eta_{ave}$) of 13.74% is obtained for this cell. The series resistance ($R_s$) also decreases with NH$_4$Cl addition (Table 1), leading to an increase in the J$_{SC}$. After standing for two weeks in ambient air, the decreases in efficiencies of cells containing NH$_4$Cl are small. A $\eta$ of 13.19% is still obtained, as shown in Table 2.

IPCE spectra of the CH$_3$NH$_3$PbI$_3$(Cl) devices were shown in Fig. 3. The CH$_3$NH$_3$PbI$_3$(Cl) cells show photoconversion efficiencies between 320 and 810 nm, which corresponds to an energy gap of 1.53 eV for the CH$_3$NH$_3$PbI$_3$. The IPCE was improved in the range of 400–700 nm by adding NH$_4$Cl, which lead to the increase of J$_{SC}$ values. Although the J$_{SC}$ values should agree with the integrated values of IPCE as previously reported in alkali metal-doped perovskite solar cells, the J$_{SC}$ values in the present work is slightly lower than the integrated values of IPCE. In order to measure the IPCE of the perovskite solar cells, DC measurements mode is better. However, the lowest frequency of the lock-in-amplifier in the present work is 4 Hz (QE-R, Enli Technology), and the lower IPCE values tended to be measured compared with the actual IPCE values. Therefore, only the wavelength region can be evaluated for the IPCE data in the present work.

OM images of the CH$_3$NH$_3$PbI$_3$(Cl) cells are shown in Fig. 4. Microparticles with sizes of 5–10 μm are observed for the cell prepared without NH$_4$Cl, as shown in Fig. 4(a). Adding NH$_4$Cl to the CH$_3$NH$_3$PbI$_3$(Cl) decreases the particle size, as shown in Fig. 4(b)–(d). In addition, networking structures with sizes of ~10 μm between microparticles are observed, especially in Fig. 4(d). These networking microstructures could potentially improve the photovoltaic properties.

A SEM image of the CH$_3$NH$_3$PbI$_3$(Cl) cell without NH$_4$Cl is shown in Fig. 5(a). Microparticles with sizes of 5–10 μm are observed on the surface of the mesoporous TiO$_2$, which correspond to those in Fig. 4(a). The particles appear have crystal facets. EDS elemental mapping images of the Pb M line, C K line, and N K line are shown in Fig. 5(b)–(f), respectively. These elemental mapping images indicate that the particles observed in Fig. 5(a) correspond to the CH$_3$NH$_3$PbI$_3$ compound. The Pb and I compositions and C : N ratio were calculated from the EDS spectrum using background correction by normalizing the peaks, and are listed in Table 3. Although the EDS values contain some errors, these results seem to

| NH$_4$Cl (mg) | Scan | J$_{SC}$ (mA cm$^{-2}$) | $V_{OC}$ (V) | FF | $\eta$ (%) | $\eta_{ave}$ (%) | $R_s$ (Ω cm$^{-2}$) |
|--------------|------|------------------------|-------------|----|------------|------------------|-------------------|
| 0            | Fw   | 21.8                   | 0.889       | 0.610 | 11.85      | 11.76            | 6.92              |
|              | Rv   | 21.5                   | 0.893       | 0.647 | 12.41      | 12.37            | 6.56              |
| 1            | Fw   | 22.4                   | 0.909       | 0.633 | 12.90      | 12.50            | 6.44              |
|              | Rv   | 22.2                   | 0.912       | 0.651 | 13.19      | 12.89            | 6.18              |
| 3            | Fw   | 22.4                   | 0.913       | 0.636 | 13.01      | 11.25            | 6.40              |
|              | Rv   | 22.5                   | 0.917       | 0.651 | 13.40      | 12.13            | 6.06              |
| 5            | Fw   | 22.6                   | 0.908       | 0.673 | 13.83      | 13.59            | 4.66              |
|              | Rv   | 22.6                   | 0.908       | 0.685 | 14.03      | 13.74            | 4.70              |

Table 1 Measured photovoltaic parameters of the CH$_3$NH$_3$PbI$_3$(Cl) solar cells

Table 2 Measured photovoltaic parameters of the CH$_3$NH$_3$PbI$_3$(Cl) solar cells after two weeks
indicate that the composition of CH$_3$NH$_3$PbI$_3$ may be I deficient. In addition, EDS indicates that C is dispersed throughout the matrix.

Fig. 6(a) shows a SEM image of the CH$_3$NH$_3$PbI$_3$Cl cell containing 5 mg of NH$_4$Cl. The surface morphology changes upon adding NH$_4$Cl to the CH$_3$NH$_3$PbI$_3$. The average particle sizes is ~5 µm, and crystals are connected to each other with special facets. These networking surface structures could potentially improve the surface coverage and therefore the photovoltaic properties. Fig. 6(b)–(f) show EDS elemental mapping images of Pb, I, Cl, C, and N, respectively. The elemental compositions and C : N ratios were calculated from the EDS spectra, and are also listed in Table 3. These data indicate that the CH$_3$NH$_3$PbI$_3$ starting composition may be I deficient. Cl would be doped into the CH$_3$NH$_3$PbI$_3$, as shown in Table 3. In Fig. 6(e), C appears to be dispersed throughout the matrix. The EDS results indicate that the I site occupancy would be <1, and that this I deficiency may increase the hole concentration. The networking surface structures are expected to affect the photovoltaic properties, in addition to the doping effect of Cl at I sites. The CH$_3$ : NH$_3$ ratio in the CH$_3$NH$_3$PbI$_3$Cl phase prepared by air blowing is almost 6 : 4. This is consistent with excess CH$_3$ compared with NH$_3$, and is caused by the air blowing procedure as shown in Table 3. Although the EDS values contain some errors, these results seem to indicate that the composition of CH$_3$NH$_3$PbI$_3$ may be I deficient. In addition, EDS indicates that C is dispersed throughout the matrix.

Fig. 7(a)–(d) shows XRD patterns of the FTO/TiO$_2$/CH$_3$NH$_3$PbI$_3$Cl/spiro-OMeTAD/Au cells. The diffraction peaks can be indexed by a cubic crystal system (Pm3m) for CH$_3$NH$_3$PbI$_3$Cl perovskite thin films. The XRD pattern of a CH$_3$NH$_3$PbI$_3$Cl cell prepared without air blowing or PbCl$_2$ is shown in Fig. 7(e). The diffraction peaks of FTO and TiO$_2$ arise from the FTO substrate and TiO$_2$ mesoporous layer, respectively. For ordinary CH$_3$NH$_3$PbI$_3$ cells prepared at 100 °C without air blowing, XRD

Table 3 Compositions of the solar cells as measured by EDS

| NH$_4$Cl (mg) | Pb (at%) | I (at%) | Cl (at%) | C : N (at%) |
|---------------|----------|---------|----------|-------------|
| 0             | 33.5     | 61.2    | 5.3      | 61.9 : 38.1 |
| 1             | 33.5     | 61.9    | 4.6      | 61.7 : 38.3 |
| 3             | 34.0     | 61.6    | 4.5      | 61.8 : 38.2 |
| 5             | 33.7     | 60.8    | 5.5      | 61.8 : 38.2 |
| 5$^a$         | 33.5     | 61.8    | 4.7      | 52.0 : 48.0 |

$^a$ No air blowing or PbCl$_2$. 

Fig. 3 IPCE spectra of CH$_3$NH$_3$PbI$_3$(Cl) solar cells with and without NH$_4$Cl.

Fig. 4 OM images of CH$_3$NH$_3$PbI$_3$(Cl) cells containing (a) 0 mg, (b) 1 mg, (c) 3 mg, and (d) 5 mg of NH$_4$Cl.

Fig. 5 (a) SEM image of the CH$_3$NH$_3$PbI$_3$(Cl) cell without NH$_4$Cl, and corresponding elemental mapping images of the (b) Pb M line, (c) I L line, (d) Cl K line, (e) C K line, and (f) N K line.
peaks of PbI₂ have been reported similarly to those in Fig. 7(e). The intensities of the 100 and 200 peaks of the perovskite phase increase by more than 100 times with air blowing and NH₄Cl, as observed in Fig. 7(b)–(d). The 100 and 200 reflections are sufficiently intense that the diffraction peaks of FTO and TiO₂ are not readily apparent.

The ratios of the 100 diffraction intensities (I₁₀₀) to the 210 diffraction intensities (I₂₁₀) of the perovskite crystals were calculated as I₁₀₀/I₂₁₀, from the XRD data in Fig. 6. The results are summarized in Table 4. If the CH₃NH₃PbI₃ cubic perovskite particles are randomly oriented, then the I₁₀₀/I₂₁₀ value should be 1.81. For the cell prepared using air blowing and without NH₄Cl, the I₁₀₀/I₂₁₀ is 61. This indicates that the (100) planes of the perovskite particles are preferentially oriented parallel to the FTO substrate. Adding NH₄Cl to the cell results in the I₁₀₀/I₂₁₀ increasing to 3600, which is 2000 times higher than the I₁₀₀/I₂₁₀ of randomly oriented perovskite crystals. The cell prepared with 5 mg of NH₄Cl without air blowing or PbCl₂ has an I₁₀₀/I₂₁₀ of 2.8. This indicates that most of the perovskite particles are randomly oriented. The ratios of the I₁₀₀ intensities to the FTO substrate intensities (I₁₀₀/IFTO) were also calculated for the perovskite crystals, and are also shown in Table 4. Using air blowing and NH₄Cl increases the I₁₀₀/IFTO. These results indicate that preferential (100) crystal orientation occurs in films prepared using air blowing with NH₄Cl. By using a least squares method, the lattice constants were determined to be 6.274, 6.276, 6.276, 6.276, and 6.275 Å for the cells with NH₄Cl 0 mg, 1 mg, 3 mg, and 5 mg, and NH₄Cl 0 mg without air blowing.

Two mechanisms are considered for the formation of the (100)-oriented CH₃NH₃PbI₃(Cl) perovskite crystals. The first mechanism is crystal growth being promoted by air blowing during spin-coating of the perovskite layers. When the CH₃NH₃PbI₃(Cl) solution crystallizes into perovskite particles, fast annealing with air flow accelerates the crystallization of
NH4Cl addition combined with an air blow method is an effective method for fabrication of highly crystalline-oriented homogeneous thin films.

**Conflicts of interest**

There are no conflicts to declare.

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