FULL PAPER

Effects of annealing on $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ perovskite photovoltaic devicesTakeo OKU^{1,†} and Yuya OHISHI¹¹Department of Materials Science, University of Shiga Prefecture, 2500 Hassaka, Hikone, Shiga 522-8533, Japan

The effects of annealing temperatures on perovskite-type photovoltaic devices were investigated. $\text{CH}_3\text{NH}_3\text{PbI}_3$ photovoltaic devices doped with Cl were fabricated by the spin-coating method, and the microstructures of the cells were investigated by X-ray diffraction, optical microscopy and scanning electron microscopy. The current density–voltage characteristics and incident photon-to-current conversion efficiencies were improved by application of an appropriate annealing process, leading to improvement of the photoconversion efficiencies to 13.28%. Microstructure analysis indicated that the perovskite layer had a homogeneous morphology after annealing at 140°C, and that the devices provided stability in air.

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1. Introduction

Thin film solar cells with perovskite-type methylammonium trihalogenoplumbates (II) ($\text{CH}_3\text{NH}_3\text{PbI}_3$) compounds have been widely studied recently due to their easy fabrication processes and high conversion efficiencies compared to conventional organic solar cells.^{1)–3)} Since a conversion efficiency of 15% was attained,⁴⁾ higher efficiencies have been accomplished for various perovskite compounds and device structures,^{5)–7)} and conversion efficiencies above 20% have been achieved.^{8)–15)}

It has been reported that the photovoltaic properties of perovskite solar cells depended heavily on the compositions and crystal structures of the perovskite compounds. Doping with metal atoms such as tin (Sn),^{16),17)} antimony (Sb),^{18)–21)} copper (Cu),²²⁾ arsenic (As),²³⁾ germanium (Ge),^{24),25)} indium (In),²⁵⁾ or thallium (Tl)²⁵⁾ at the lead (Pb) sites have been performed. The optical absorption ranges of the perovskite compounds were expanded by Sn or Tl doping,^{16),17),25)} and the photoconversion efficiencies of the perovskite solar cells were improved by Sb, Cu or As doping.^{18)–23)} Doping with such other elements as cesium,⁹⁾ rubidium¹³⁾ or formamidinium ($\text{NH}=\text{CHNH}_3$, FA)^{8),11)} at the methylammonium (MA) sites also improved the conversion efficiencies.

Studies on doping with halogen atoms, such as chlorine (Cl)^{26)–34)} or bromine (Br),^{11),21)} at the iodine (I) sites of the perovskite crystals have also been reported. The doped Cl ions were found to lengthen the diffusion length of excitons, which resulted in improvement of the conversion efficiency.^{26),35)} Further studies on metal, halogen, and/or FA doping at the Pb, I and/or MA sites are fascinating for

their effects on the photovoltaic properties and microstructures of the perovskite solar cells.³⁴⁾

The purpose of the present work was to investigate the effects of annealing on perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ photovoltaic devices doped with Cl, which is denoted as $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ in the present work. The Cl element is expected to increase the carrier diffusion length in the perovskite crystals,^{26),35)} and the annealing temperatures should affect both the microstructures and photovoltaic properties of the perovskite solar cells.³⁶⁾ The effects of annealing temperatures on the formation of perovskite compounds for the photovoltaic cells were investigated by light-induced current density–voltage (J – V) characteristics, incident photon-to-current conversion efficiency (IPCE), X-ray diffraction (XRD), optical microscopy, and scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDS).

2. Experimental procedures

Figure 1 is a schematic illustration of the fabrication of the present $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ photovoltaic cells. Details of the basic fabrication process are described in published reports,^{18),29),32)} except that for Cl-doping. F-doped tin oxide (FTO) substrates were cleaned using an ultrasonic bath with acetone and methanol, and dried under nitrogen gas. 0.15 and 0.30 M TiO_2 precursor solution was prepared from titanium diisopropoxide bis(acetylacetonate) (Sigma-Aldrich, 0.055 and 0.11 mL) with 1-butanol (1 mL), and the 0.15 M TiO_2 precursor solution was spin-coated on the FTO substrate at 3000 rpm for 30 s and heated at 125°C for 5 min in air to form a TiO_x layer. The 0.30 M TiO_2 precursor solution was spin-coated onto the TiO_x layer at 3000 rpm for 30 s, and heated at 125°C for 5 min. This process of coating with a 0.30 M solution was

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Fig. 1. Schematic illustration of the fabrication of $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ photovoltaic cells.

then performed two times, and the FTO substrate was annealed at 500°C for 30 min to form a compact TiO_2 layer. For the mesoporous TiO_2 layer, TiO_2 paste was prepared with TiO_2 powder (Nippon Aerosil, P-25) with poly(ethylene glycol) (Nacalai Tesque, PEG #20000) in ultrapure water. The solution was mixed with acetylacetone (Wako Pure Chemical Industries, 10 μL) and triton X-100 (Sigma-Aldrich, 5 μL) for 30 min, and then left for 12 h to suppress the bubbles in the solution. After that, the TiO_2 paste was coated onto the substrate by spin-coating at 5000 rpm for 30 s. The cells were then annealed at 120°C for 5 min and at 500°C for 30 min to form a mesoporous TiO_2 layer.

For the preparation of perovskite compounds, a solution of $\text{CH}_3\text{NH}_3\text{I}$ (Showa Chemical Co., Ltd., 190.7 mg) and PbCl_2 (Sigma-Aldrich, 111.2 mg) was prepared with a mole ratio of 3:1 in N,N -dimethylformamide (Nacalai Tesque, 500 μL) at 60°C for 24 h.^{27,28,33} The solution of $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ was introduced into the TiO_2 mesopores by the spin-coating method and annealed at ~150°C for 10 min to form the perovskite layer. A hole transport layer (HTL) was then prepared by spin-coating onto the perovskite layer. For the hole transport layer, a solution 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) was mixed with a solution of lithium bis(trifluoromethylsulfonyl)imide (Li-TFSI, Tokyo Chemical Industry, 260 mg) in acetonitrile (Nacalai Tesque, 0.5 mL) for 12 h. The former solution with 4-tert-butylpyridine (Aldrich, 14.4 μL) was mixed with the Li-TFSI solution (8.8 μL) for 30 min at 70°C. All procedures for preparation of the thin

Fig. 2. J - V characteristic of $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ photovoltaic cells.

films were performed in ambient air. Finally, gold (Au) contacts were evaporated as top metal electrodes. The layered structures of the present solar cells were denoted FTO/ TiO_2 / $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ /spiro-OMeTAD/Au, as shown in Fig. 1.

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). The J - V measurements were performed by source measure unit (Keysight, B2901A Precision SMU). The scan rate and sampling time were ~0.08 V s^{-1} and 1 ms, respectively, and averaged values of the forward and reverse scans were used as the photovoltaic parameters. Four cells were tested for each condition. The solar cells were illuminated through the sides of the FTO substrates, and the illuminated area was 0.090 cm^2 . The IPCE of the cells were also measured (Enli Technology, QE-R). The microstructures of the present 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.

3. Results and discussion

Figure 2 shows the J - V characteristics of the TiO_2 / $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ /spiro-OMeTAD photovoltaic cells under illumination, which indicate the effects of the annealing temperatures. Forward and reverse scans are indicated by the solid and dotted lines, respectively. The measured photovoltaic parameters of the TiO_2 / $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ cells are summarized in Table 1. Small hysteresis was observed for the J - V characteristics, and the averaged values are listed in Table 1. Since a small amount of carriers might be generated and charged in the TiO_2 layer during J - V measurements under light irradiation and current flow, the electrical resistance would be reduced and the photocurrent increased, which would result in a hysteresis curve. The perovskite would also have hysteresis properties among its J - V characteristics.³⁷⁾

Table 1. Measured photovoltaic parameters (top and average) of $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ cells

Annealing (°C)	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	η_{top} (%)	η_{ave} (%)
100*	15.9	0.786	0.514	6.42	6.21
130	19.9	0.924	0.626	11.49	11.07
140	20.1	0.958	0.690	13.28	12.27
150	17.9	0.903	0.556	8.98	7.51
After 7 days					
130	19.1	0.891	0.590	10.04	9.32
140	19.2	0.924	0.664	12.11	11.12
150	14.9	0.696	0.218	2.27	1.74

* $\text{CH}_3\text{NH}_3\text{PbI}_3$ (without Cl). **Fig. 3.** IPCE spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ cells.

Ordinary $\text{CH}_3\text{NH}_3\text{PbI}_3$ cells annealed at 100°C provided a power conversion efficiency (η) of 6.42%, and the averaged efficiency (η_{ave}) of four electrodes on the cells is 6.21%, as listed in Table 1. For the Cl-doped $\text{CH}_3\text{NH}_3\text{PbI}_3$, the short-circuit current density (J_{SC}), open-circuit voltage (V_{OC}) and fill factor (FF) were increased by annealing at 130°C , and an η of 11.49% was obtained. After annealing at 140°C , the highest efficiency was obtained for the $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ cell, which provided an η of 13.28%, a FF of 0.690, a J_{SC} of 20.1 mA cm^{-2} , and a V_{OC} of 0.958 V. The highest average-efficiency was obtained for this cell, which provided an η_{ave} of 12.27%. The photovoltaic parameters were deteriorated by further annealing at 150°C , and the η decreased to 8.98%, as shown in Table 1.

After 7 days, the decrease in the efficiencies of the cells annealed at 140°C remained small, and an η of 12.11% was still preserved for the best cell, as shown in Table 1. Although the efficiencies of the devices were nearly stable during the J - V measurements in the present work, durability tests of long-time use should be carried out in preparation for practical application of the perovskite solar cells in the future.

Figure 3 shows IPCE spectra of the $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ devices. The $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ cells show photoconversion efficiencies between 320 and 800 nm, which corresponds

Fig. 4. Optical microscopic images (a)–(c) and SEM images (d)–(f) of $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ cells annealed at (a, d) 130°C , (b, e) 140°C and (c, f) 150°C , respectively.

to an energy gap of 1.55 eV for the $\text{CH}_3\text{NH}_3\text{PbI}_3$.³⁴⁾ The IPCE was improved in the range of 400–750 nm by annealing at 140°C . In the present work, the energy gap of the $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ phase was almost the same as that of the ordinary $\text{CH}_3\text{NH}_3\text{PbI}_3$ phase, which might indicate a small Cl composition.

Optical microscopic images of $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ cells are shown in **Figs. 4(a)–4(c)**. Homogeneous structures are observed for the cells annealed at 130 and 140°C , as shown in Figs. 4(a) and 4(b), compared with the ordinary $\text{CH}_3\text{NH}_3\text{PbI}_3$ cells.^{19),32)} These homogeneous microstructures would improve the photovoltaic properties as well as the doping effect of Cl at the I sites. After annealing at 150°C , the morphology was drastically changed, as shown in Fig. 4(c).

SEM images of $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ cells annealed at 130, 140 and 150°C are shown in Figs. 4(d)–4(f), respectively. Homogeneous structures are observed for the cells annealed at 130°C , as shown in Fig. 4(d). During annealing at 140°C , large numbers of particles a few micrometers in size appeared on the surface of the cell, as shown in Fig. 4(e). After annealing at 150°C , a different type of microstructure is observed. The particles in appearing Fig. 4(e) grew to cover the surface of the cell, which indicates the formation of other compounds on the surface of the cell.

Based on the SEM-EDS spectrum of the $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ cell annealed at 140°C , the composition ratios were calculated as $\text{Pb:I:Cl} = 34.4:60.4:5.2$ and $\text{C:N} = 52.3:47.7$. These results indicate that Cl and I might be deficient from the starting composition of $(\text{CH}_3\text{NH}_3)_3\text{PbI}_3\text{Cl}_2$, and the deficient I would increase the hole concentration. It is considered that the surface structures

Fig. 5. XRD patterns of $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ cells.

would significantly affect the photovoltaic properties, in addition to the doping effect of Cl at the I sites.

Figure 5 shows XRD patterns of FTO/ TiO_2 / $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ cells annealed at 130, 140 and 150°C. The diffraction peaks indicated by FTO and TiO_2 are from the FTO substrate and TiO_2 mesoporous layer, respectively. The diffraction reflections can be indexed by a cubic crystal system ($Pm\bar{3}m$) for $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ perovskite thin films. The peak intensities of 100 of the perovskite phase increased with annealing at elevated temperatures. Most notably, the 200 reflection of the perovskite provided the highest intensity after annealing at 140°C, which indicated crystal growth of the perovskite phase.

Along with XRD peaks of the perovskite structure, a small diffraction peak corresponding to the PbI_2 compound appeared for the cell annealed at 140°C, which corresponded to the formation of microparticles on the surface of the device, as observed in Fig. 4(e). After annealing at 150°C, the diffraction intensity of PbI_2 increased slightly, and the intensity of the 200 reflection of the perovskite decreased. This would indicate a small amount of separation of PbI_2 from the $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ perovskite crystal, and a resulting significant changes in the surface structures, as observed in Figs. 4(c) and 4(f).

For ordinary $\text{CH}_3\text{NH}_3\text{PbI}_3$ cells prepared at 100°C, XRD peaks of PbI_2 have sometimes been observed.^{34),36)} The XRD results for $\text{CH}_3\text{NH}_3\text{PbI}_3$ in Fig. 5 showed the formation of PbI_2 after annealing at 150°C for 10 min, which would indicate partial separation of PbI_2 from $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ after high-temperature annealing. Although a small amount of PbI_2 might be effective for conversion

efficiency,¹¹⁾ further formation of PbI_2 would deteriorate the photovoltaic properties, with a resulting decrease in conversion efficiencies after annealing at 150°C, as indicated in Table 1.

The 100/200 peak intensity ratios for samples annealed at 130, 140 and 150°C were calculated as 1.98, 2.15, and 2.87, respectively. The ratios should be the same (~ 1.81) if the perovskite structures preserve the original space group ($Pm\bar{3}m$).³⁴⁾ The crystal symmetry may have deteriorated, therefore due to the separation of PbI_2 from $\text{CH}_3\text{NH}_3\text{PbI}_3$ with annealing at above 140°C. On the other hand, the 200/210 peak intensity ratios for the samples annealed at 130, 140 and 150°C were calculated as 1.45, 3.37, and 2.87, respectively. This indicates that there may be some preferred crystal orientation in the samples, and that the preferred orientation might be related to the surface and interfacial structures.

Two assumed mechanisms could be considered for the increase in the photoconversion efficiencies. The first is Cl-doping at the I site. Excess molecules of $2(\text{CH}_3\text{NH}_3\text{Cl})$ might be vaporized from the starting composition of $3(\text{CH}_3\text{NH}_3\text{I}) + \text{PbCl}_2$.^{27),28),33)} When a small amount of remaining Cl was doped in the $\text{CH}_3\text{NH}_3\text{PbI}_3$ phase, as detected by EDS analysis, the diffusion length of excitons would be lengthened by the doped Cl atoms,^{26),35)} with a resulting increase in the J_{SC} values.

The second mechanism is formation of homogeneous morphologies, such as surface and interface structures, of the perovskite layers by appropriate annealing conditions and Cl-doping.^{19),32)} The microstructure analyses of the photovoltaic cells prepared at 140°C indicated that the perovskite layer had a homogeneous morphology, which improved its photovoltaic properties, especially the J_{SC} and FF values. Detailed research is required for specific nanostructure analysis of the devices.

4. Conclusion

Effects of annealing temperatures on perovskite-type $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ photovoltaic devices were investigated. $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ -based cells were fabricated by a spin-coating technique, and the J - V characteristics and IPCE were improved by a suitable annealing process, which resulted in improvement of the conversion efficiencies to above 13% and stability of the device in air. The microstructures of the cells were investigated by optical microscopy, SEM-EDS and XRD, and microstructure analysis indicated that the perovskite layer had a homogeneous morphology with high crystallinity after annealing at 140°C.

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