Effects of NH₄Cl addition to perovskite CH₃NH₃PbI₃ photovoltaic devices

Takeo OKU†, Yuya OHISHI, Atsushi SUZUKI and Yuzuru MIYAZAWA*

Department of Materials Science, University of Shiga Prefecture, 2500 Hassaka, Hikone, Shiga 522–8533, Japan
†U-TEC Laboratory, U-TEC Corporation, 648–1 Matsukasa, Yamato-ku, Nara 639–1124, Japan

Effects of NH₄Cl addition to perovskite CH₃NH₃PbI₃ precursor solutions on photovoltaic properties were investigated. TiO₂/CH₃NH₃PbI₃(Cl) photovoltaic devices were fabricated by a spin-coating technique, and the microstructures of the devices were investigated by X-ray diffraction and scanning electron microscopy. Current density–voltage characteristics were improved by a small amount of Cl-doping, which resulted in improvement of the efficiencies of the devices. The structure analysis indicated formation of a homogeneous microstructure by NH₄Cl addition to the perovskite phase, and formation of PbI₂ was suppressed by the NH₄Cl addition.

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Key-words : Microstructure, Photoconversion, Solar cell, Perovskite, NH₄Cl

1. Introduction

Perovskite-type methylammonium trihalogenoplumbates (II) (CH₃NH₃PbI₃, MAPbI₃) solar cells have been extensively studied owing to its easy fabrication process and the high conversion efficiencies compared to the common organic solar cells. After a conversion efficiency reached 15% in 2013, higher efficiencies have been achieved for various device structures and processes, and the conversion efficiency increased above 20% recently.

The photovoltaic properties of the perovskite solar cells are fairly dependent on compositions and the crystal structures of the perovskite compounds. Halogen atom doping, such as bromine (Br) or chlorine (Cl), at the iodine (I) sites of the perovskite crystals have been investigated. The doped Cl ions could lengthen the diffusion length of excitons, which resulted in the improvement in the conversion efficiency. In our previous work, PbCl₂ were added to the CH₃NH₃PbI₃, which resulted in the improvement CH₃NH₃PbI₃, and the highest conversion efficiency was obtained for the CH₃NH₃PbI₂.88Cl0.12 cell.

In addition, studies on metal atom doping, such as tin (Sn), germanium (Ge), antimony (Sb), arsenic (As), or thallium (Tl) at the lead (Pb) sites have been performed. The optical absorption ranges of the perovskite solar cells were expanded by Sn or Ti-doping, and the photoconversion efficiencies were improved by Sb-doping. Further doping of cesium or formamidinium (NH₄) also improved the conversion efficiencies of the perovskite solar cells. Detailed studies on the halogen, metal and/or FA doping at the I, Pb and/or CH₃NH₃ sites are intriguing for effects on the photovoltaic properties and microstructures.

The purpose of the present work is to investigate photovoltaic properties and microstructures of perovskite-type CH₃NH₃PbI₃(Cl) photovoltaic devices, which were prepared by a spin-coating technique in air. The Cl element is expected to increase the carrier diffusion length in the perovskite crystals, and an improvement of the morphology and crystallinity of the thin films is also expected by adding NH₄Cl. The effects of NH₄Cl addition using a mixture solution of perovskite compounds on the photovoltaic properties and microstructures were investigated by light-induced current density–voltage (J–V) characteristics, incident photon-to-current conversion efficiency (IPCE), X-ray diffraction (XRD), and scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDS).

2. Experimental procedures

A schematic illustration for the fabrication of the present TiO₂/CH₃NH₃PbI₃(Cl) photovoltaic cells is shown in Fig. 1. The details of the fabrication process are described in the reported papers, except for NH₄Cl. 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 TiO₂ 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 TiO₂ precursor solution was spin-coated on the FTO substrate at 3000 rpm for 30 s, and annealed at 125°C for 5 min. Then, the 0.3 M TiO₂ precursor solution was spin-coated on the TiO₂ layer at 3000 rpm for 30 s, and annealed at 125°C for 5 min. This process of 0.30 M solution was performed two times, and the FTO substrate was sintered at 500°C for 30 min to form the compact TiO₂ layer. After that, TiO₂ paste was coated on the substrate by spin-coating at 5000 rpm for 30 s. For the mesoporous TiO₂ layer, the TiO₂ paste was prepared with TiO₂ powder (Nippon Aerosil, P-25) with poly(ethylene glycol) (Nacalai Tesque, PEG #20000) in ultrapure water. The solution was mixed with acetylacetonate (Wako Pure Chemical Industries, 10μL) and triton X-100 (Sigma-Aldrich, 5μL) for 30 min, and was left for 12 h to suppress the bubbles in the solution. The cells were annealed at 120°C for 5 min and at 500°C for 30 min to form the mesoporous TiO₂ layer. For the preparation of the perovskite compounds, a solution of CH₃NH₃I (Showa Chemical Co., Ltd., 98.8 mg), PbI₂ (Sigma-Aldrich, 289.3 mg), and NH₄Cl (Wako Pure Chemicals Industries, Ltd.) was prepared with a
desired mole ratio in mixture of N,N-dimethyldiformamide (DMF, Nacalai Tesque, 225 µL) and γ-butyrolactone (Nacalai Tesque, 275 µL) at 60°C. Addition of the DMF to γ-butyrolactone is expected to improve the photovoltaic properties.\(^{23,24,28}\) The preparation compositions of TiO\(_2\)/CH\(_3\)NH\(_3\)PbI\(_3\)(Cl) cells with a NH\(_4\)Cl additive are listed in Table 1. The solution of CH\(_3\)NH\(_3\)-PbI\(_3\)(Cl) was introduced into the TiO\(_2\) mesopores by a spin-coating method and annealed at 100°C for 15 min. Then, a hole transport layer (HTL) was prepared by spin-coating. For the hole transport layer, a solution of 2,2',7,7'-tetrakis[N,N-di(p-methoxyphenyl)amine]-9,9'-spirobifluorene (spiro-OMeTAD, Wako Pure Chemical Industries, 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 30 min. The former solution with 4-tert-butylpyridine (Aldrich, 14.4 mg) was mixed with the Li-TFSI solution (8.8 µL) at 60°C. Addition of the DMF to γ-butyrolactone is expected to improve the photovoltaic properties.\(^{23,24,28}\) The preparation compositions of TiO\(_2\)/CH\(_3\)NH\(_3\)PbI\(_3\)(Cl) cells with a NH\(_4\)Cl additive are listed in Table 1. The solution of CH\(_3\)NH\(_3\)-PbI\(_3\)(Cl) was introduced into the TiO\(_2\) mesopores by a spin-coating method and annealed at 100°C for 15 min. Then, a hole transport layer (HTL) was prepared by spin-coating. For the hole transport layer, a solution of 2,2',7,7'-tetrakis[N,N-di(p-methoxyphenyl)amine]-9,9'-spirobifluorene (spiro-OMeTAD, Wako Pure Chemical Industries, 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 30 min. The former solution with 4-tert-butylpyridine (Aldrich, 14.4 mg) was mixed with the Li-TFSI solution (8.8 µL) at 60°C. Addition of the DMF to γ-butyrolactone is expected to improve the photovoltaic properties.\(^{23,24,28}\) The preparation compositions of TiO\(_2\)/CH\(_3\)NH\(_3\)PbI\(_3\)(Cl) cells with a NH\(_4\)Cl additive are listed in Table 1. The solution of CH\(_3\)NH\(_3\)-PbI\(_3\)(Cl) was introduced into the TiO\(_2\) mesopores by a spin-coating method and annealed at 100°C for 15 min. Then, a hole transport layer (HTL) was prepared by spin-coating. For the hole transport layer, a solution of 2,2',7,7'-tetrakis[N,N-di(p-methoxyphenyl)amine]-9,9'-spirobifluorene (spiro-OMeTAD, Wako Pure Chemical Industries, 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 films were performed in ordinary air. Lastly, gold (Au) contacts were evaporated as top metal electrodes. Layered structures of the present solar cells were denoted as FTO/TiO\(_2\)/CH\(_3\)NH\(_3\)PbI\(_3\)(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\(^{-2}\) 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 illuminated area was 0.090 cm\(^2\). The IPCE of the cells were also measured (Enli Technology, QE-R). The microstructures of the thin film devices were investigated by using an X-ray diffractometer (Bruker, D2 PHASER), and a scanning electron microscope (Jeol, JSM-6010PLUS/LA) equipped with EDS.

### Results and discussion

The \(J\)-\(V\) characteristics of the TiO\(_2\)/CH\(_3\)NH\(_3\)PbI\(_3\)(Cl)/spiro-OMeTAD photovoltaic cells under illumination are shown in Fig. 2, which indicates an effect NH\(_4\)Cl addition to the CH\(_3\)NH\(_3\)-PbI\(_3\). The measured photovoltaic parameters of the TiO\(_2\)/CH\(_3\)NH\(_3\)PbI\(_3\)(Cl) cells are summarized in Table 2. The CH\(_3\)NH\(_3\)-PbI\(_3\) cell provided the highest power conversion efficiency (\(\eta_{max}\)) of 7.05%, and the averaged efficiency (\(\eta_{ave}\)) of three electrodes on the cells is 6.66%, as listed in Table 2. A short-circuit current density \(J_{SC}\) increased up to 21.4 mA cm\(^{-2}\) by an addition of 25 mg NH\(_4\)Cl, which would indicate an increase of carrier diffusion length. The highest efficiency was obtained for a cell added with 35 mg NH\(_4\)Cl, which provided the \(\eta_{max}\) of 9.63%, a fill factor (\(FF\)) of 0.536, a \(J_{SC}\) of 19.9 mA cm\(^{-2}\), and an open-circuit voltage \(V_{OC}\) of 0.903 V. The highest average-efficiency was obtained for a cell added with 25 mg NH\(_4\)Cl, which provided an \(\eta_{ave}\) of 9.22%.

IPCE spectra of the CH\(_3\)NH\(_3\)PbI\(_3\) and CH\(_3\)NH\(_3\)PbI\(_3\)(Cl) cells added with 30 mg NH\(_4\)Cl are shown in Fig. 3. The CH\(_3\)NH\(_3\)-PbI\(_3\)(Cl) device shows photoversion efficiencies between 300 and 800 nm, which corresponds to an energy gap of 1.55 eV for the CH\(_3\)NH\(_3\)PbI\(_3\). The IPCE was improved in the range of 450-
750 nm by the addition of NH4Cl to the CH3NH3PbI3. In the present work, the energy gaps of the CH3NH3PbI3(Cl) phase were almost constant even by the Cl-doping, which agreed well with the constant values of the open-circuit voltages.

XRD patterns of FTO/TiO2/CH3NH3PbI3(Cl) devices are shown in Fig. 4. The diffraction peaks can be indexed by a cubic crystal system (Pm3m) for the CH3NH3PbI3(Cl) thin films. In addition to XRD peaks of the ordinary perovskite structure, broader diffraction peaks due to the PbI2 compound appeared in the CH3NH3PbI3(Cl) film, as shown in Fig. 4. However, the NH4Cl addition suppressed the formation of PbI2, and peak intensities of 100 of the perovskite phase increased.

The XRD result of CH3NH3PbI3 in Fig. 4 also showed the existence of PbI2 after annealing at 100°C for 15 min. This would indicate partial separation of PbI2 from CH3NH3PbI3 after annealing, and the formation of PbI2 was suppressed by the NH4Cl addition, which would result in the increase of conversion efficiencies of the devices.

A SEM image of TiO2/CH3NH3PbI3 cell without NH4Cl is shown in Fig. 5(a). Perovskite crystals with sizes of 5–10 μm are observed at the surface of the mesoporous TiO2, and the crystals have a star-like shape. Elemental mapping images of Pb, I, C, and N by SEM-EDS are shown in Figs. 5(b)–5(e), respectively. The elemental mapping images indicate the particles observed in Fig. 5(a) correspond to the CH3NH3PbI3 compound. The composition ratios of elements Pb, I, and C:N were calculated from the EDS spectrum using background correction by normaliz-
ing the spectrum peaks, as listed in Table 3. This result indicates that I might be deficient from the starting composition of CH$_3$NH$_3$PbI$_3$, and the deficient I might increase the hole concentration. In addition, carbon atoms are dispersed in the matrix.

Figure 6(a) is a SEM image of TiO$_2$/CH$_3$NH$_3$PbI$_3$(Cl) cell with 5 mg NH$_4$Cl additive. The surface morphology was drastically changed by the addition of NH$_4$Cl to the CH$_3$NH$_3$PbI$_3$. The particle sizes are a few μm, and the crystals have a round shape. The composition ratios of metal elements and C:N were calculated from the EDS spectrum, as listed in Table 3, which indicates that I might be deficient from the starting composition of CH$_3$NH$_3$PbI$_3$. On the other hands, Cl element would be appropriately doped in the CH$_3$NH$_3$PbI$_3$, as listed in Table 3. In Fig. 6(c), carbon atoms seem to be dispersed homogeneously.

Figure 7(a) is a SEM image of CH$_3$NH$_3$PbI$_3$(Cl) cell added with 25 mg NH$_4$Cl. By adding 25 mg NH$_4$Cl to the CH$_3$NH$_3$PbI$_3$, the crystal morphology was extremely changed, and no special crystal shape is observed, which would be due to an effect of NH$_4$Cl addition. Elemental mapping images of Pb M line, I L line, Cl K line, C K line, and N K line are shown in Figs. 7(b)–7(f), respectively, and the images indicate the perovskite CH$_3$NH$_3$PbI$_3$ phase is dispersed homogeneously on the photovoltaic device. These homogeneous surface structures would improve the photovoltaic properties. From the SEM-EDS results, site occupancies of I atom would also be less than 1, which might be due to the partial separation of PbI$_2$ from the CH$_3$NH$_3$PbI$_3$ phase. The composition of NH$_3$ also seem to be deficient compared with that of the CH$_3$, and it became almost constant by the NH$_4$Cl addition, which would indicate the NH$_3$ are doped at the vacant NH$_3$ positions.

Three assumed mechanisms could be considered for the increase of the photoconversion efficiencies. The first mechanism is as follows: when a small amount of Cl was doped in the CH$_3$NH$_3$PbI$_3$ phase, diffusion length of excitons would be lengthened by the doped Cl atoms,$^{12,15}$ which would result in the increase of the $J_{SC}$ values. The second is as follows: the homogeneous surface and interfacial structures formed by adding NH$_4$Cl to the CH$_3$NH$_3$PbI$_3$, which improved the photovoltaic properties, especially the FF values. The third is as follows: the deficient NH$_3$ positions are filled with NH$_3$ from NH$_4$Cl, which would lead to the stable perovskite structure by suppression of PbI$_2$ separation. Further studies are mandatory for precise structure determination of the devices.

The photovoltaic performance of the cell containing more than 35 mg was deteriorated, as listed in Table 2. This would be due to increase of series resistance by the remained undoped Cl element in the perovskite phase and undetermined compounds, which were observed as small XRD peaks around 22 and 32.5° for NH$_4$Cl 45 mg added sample in Fig. 4.

| NH$_4$Cl (mg) | Pb (at.%) | I (at.%) | Cl (at.%) | C:N (at.%)
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![Table 3. Measured compositions of TiO$_2$/CH$_3$NH$_3$PbI$_3$(Cl) cells](image-url)
4. Conclusion

The effects of NH₄Cl addition to perovskite CH₃NH₃PbI₃ precursor solutions on photovoltaic properties were investigated. TiO₂/CH₃NH₃PbI₃(Cl)-based photovoltaic devices were fabricated, and the microstructures of the devices were investigated by XRD and SEM-EDS. J-V characteristics and IPCE were improved by the NH₄Cl addition to perovskite CH₃NH₃PbI₃ precursor solutions. The structural analysis also indicated the formation of a homogeneous microstructure by NH₄Cl addition, which improved the FF values and photoconversion efficiencies. The IPCE spectrum of the CH₃NH₃PbI₃(Cl) cell was also improved by the NH₄Cl addition, and showed effective carrier-generation in the range of 300 and 800 nm.

Acknowledgements This work was partly supported by Satellite Cluster Program of the Japan Science and Technology Agency, and a Grant-in-Aid for Scientific Research (C) 25420760.

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