Effects of chlorine addition to perovskite-type CH$_3$NH$_3$PbI$_3$ photovoltaic devices

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Effects of PbCl$_2$ addition to perovskite CH$_3$NH$_3$PbI$_3$ precursor solutions on the photovoltaic properties were investigated. TiO$_2$–CH$_3$NH$_3$PbI$_3$–Cl-based photovoltaic devices were fabricated, and the microstructures of the devices were investigated by X-ray diffraction. The structure analysis indicated phase transformation of the perovskite structure from cubic to tetragonal system by chlorine (Cl)-doping. External and internal quantum efficiencies were improved by a small amount of Cl-doping, which resulted in improvement of the efficiencies of the devices. This would be due to preservation of the cubic CH$_3$NH$_3$PbI$_3$–Cl structure, and to expansion of energy gap and diffusion length of excitons by Cl-doping at the iodine sites.

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1. Introduction

Organic–inorganic hybrid solar cells with perovskite-type pigments have been widely studied. Organic solar cells consisting of a CH$_3$NH$_3$PbI$_3$ compound with a perovskite structure have higher photoconversion efficiencies and stability compared with ordinary organic solar cells. Since a conversion efficiency of 15% was achieved, higher efficiencies have been reported for various device structures and processes. The photoconversion efficiency was increased up to 19–20%. The photovoltaic properties of solar cells are strongly dependent on the crystal structures of the perovskite compounds and halogen doping such as chlorine (Cl) and bromine (Br) in the perovskite compounds. The electronic structures such as energy band gaps and carrier transport would be affected by the perovskite structures, and a detailed analysis of them is mandatory.

The purpose of the present work is to investigate microstructures and photovoltaic properties of photovoltaic devices with perovskite-type CH$_3$NH$_3$PbI$_3$–Cl compounds, which were prepared by a simple spin-coating technique in air. Effects of Cl-doping using a mixture solution of perovskite compounds on the microstructures and photovoltaic properties were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDX), light-induced current density voltage (J–V) curves, external quantum efficiency (EQE) and internal quantum efficiency (IQE).

2. Experimental procedures

A schematic illustration for the fabrication of the present TiO$_2$–CH$_3$NH$_3$PbI$_3$–Cl photovoltaic cells is shown in Fig. 1. The details of the fabrication process are described in the reported paper except for the mesoporous TiO$_2$ layer. F-doped tin oxide (FTO) substrates were cleaned using an ultrasonic bath with acetone and methanol, and dried under nitrogen gas. 0.15 M TiO$_2$ precursor solution was prepared from titanium isopropoxide bis(acetyl acetonate) (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 annealed 125°C for 5 min. Then, the 0.30 M TiO$_2$ precursor solution was spin-coated on the TiO$_2$ layer at 3000 rpm for 30 s and annealed 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 TiO$_2$ layer. After that, the TiO$_2$ paste was coated on the substrate by spin-coating at 5000 rpm for 30 s. For the mesoporous TiO$_2$ layer, the TiO$_2$ paste was prepared with TiO$_2$ powder (Aerosil, P-25) with poly(ethylene glycol) (Nacalai tesque, PEG #2000) in ultrapure water. The solution was mixed with acetylactone (Wako Pure Chemical Industries, 10 µL) and triton X-100 (Sigma Aldrich, 5 µL) 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 300°C for 30 min to form the mesoporous TiO$_2$ layer. For the preparation of the perovskite compounds, a solution of CH$_3$NH$_3$I (Showa Chemical Co. Ltd., 98.8 mg), PbI$_2$ (Sigma Aldrich) and PbCl$_2$ (Sigma Aldrich) with a desired mole ratio in y-butyrolactone (Nacalai tesque, 0.5 mL) was mixed at 70°C. For a CH$_3$NH$_3$PbI$_3$–Cl$_2$ sample, a solution in N,N-dimethylformamide (DMF, Nacalai tesque, 0.5 mL) was mixed at room temperature. The solution of CH$_3$NH$_3$PbI$_3$–Cl$_2$ was then introduced into the TiO$_2$ mesopores by a spin-coating method and annealed.

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at 100°C for 15 min. Then, a hole transport layer (HTL) was prepared by spin-coating. As the HTL, a solution of 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)-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(trifluoromethanesulfonyl)imide (Li-TFSI, Tokyo Chemical Industry, 0.5 mL) for 12 h. The former solution with 4-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (Aldrich, 14.4 mL) was mixed with the Li-TFSI solution (8.8 mL) for 30 min at 70°C. All procedures were carried out in air. Finally, gold (Au) metal contacts were evaporated as top electrodes. Layered structures of the present photovoltaic cells were denoted as FTO/TiO2/CH3NH3PbI2.65Cl0.35, as shown in a schematic illustration of Fig. 1.

The J–V characteristics (Hokuto Denko HSV-110) of the photovoltaic cells were measured under illumination at 100 mW cm−2 by using an AM 1.5 solar simulator (San-er Electric XES-301S). The solar cells were illuminated through the side of the FTO substrates, and the illuminated area was 0.16 cm². The scan rate and sampling interval were 0.01 V s⁻¹ and 0.1 s, respectively, and a forward scan was used in recording the J–V curves. Four cells were tested for each condition Optical absorption of the thin films was investigated by spectrophotometer (Jasco, V-770) using the transmission spectra. The EQE and IQE of the cells were also investigated (Enli Technology, QE-R). The microstructures of the thin films were investigated by using an X-ray diffractometer (Bruker, D2 PHASER) and a scanning electron microscope (Hitachi, S-3200N) operated at 200 kV, equipped with an EDX detector (Horiba, EMAX-7000).

3. Results and discussion

The J–V characteristics of the TiO2/CH3NH3PbI2.65Cl0.35/spiro-OMeTAD photovoltaic cells under illumination are shown in Fig. 2(a), which indicates an effect of Cl-doping to the CH3NH3PbI layer. Measured photovoltaic parameters of TiO2/CH3NH3PbI, Cl cells are summarized as Table 1. The CH3NH3PbI cell provided a power conversion efficiency (η) of 6.16%, and the averaged efficiency (ηave) of four electrodes on the cells is 5.53%, as listed in Table 1. The highest efficiency was obtained for the CH3NH3PbI.30Cl.12 cell, which provided an η of 8.16%, a fill factor (FF) of 0.504, a short-circuit current density (JSC) of 18.6 mA cm⁻², and an open-circuit voltage (VOC) of 0.869 V. As a Cl composition increased, the JSC and VOC decreased, as shown in Fig. 2(b) and Table 1. Energy gaps (Eg) of CH3NH3PbI, CH3NH3PbI.30Cl.12, and CH3NH3PbI.25Cl.12 were estimated to be 1.578, 1.590 and 1.593, respectively, from the optical absorption, which indicated the energy gap of CH3NH3PbI increased by the Cl-doping.

XRD patterns of CH3NH3PbI2.65Cl0.35 thin films on the FTO/TiO2 are shown in Fig. 3(a). The temperature for XRD measurements was ~292 K. The diffraction peaks can be indexed by cubic and tetragonal crystal systems for CH3NH3PbI and CH3NH3PbI.12Cl.12 films, respectively. Although the deposited films are a single perovskite phase, broader diffraction peaks due to PbI2 compound appeared in the CH3NH3PbI film, as shown in Fig. 3(a). Figure 3(b) is enlarged XRD patterns at 2θ of ~28.5°. A diffraction peak of 200 for the CH3NH3PbI split into diffraction peaks of 004/220 for the CH3NH3PbI.12Cl.2 by the heavy Cl-doping, which indicates the structural transformation from the cubic to tetragonal crystal systems, as shown in Figs. 3(c) and 3(d), respectively. The heavy Cl-doping suppressed the formation of PbI2, and no PbCl2 was detected for the CH3NH3PbI.12Cl.2. For the CH3NH3PbI.25Cl.12, a small shoulder is observed just left of the 200 reflection as shown in Fig. 3(b), which would be due to the pseud-cubic structure between the cubic and tetragonal phases. The measured structural parameters of the CH3NH3PbI2.65Cl0.35 films are summarized in Table 2.

Figure 4(a) is a SEM image of TiO2/CH3NH3PbI2.65Cl0.12, which indicates particles with the sizes of ~10 μm. Element mapping images of Pb, I, and Cl by SEM-EDX are shown in Figs. 4(b)–4(d), respectively. The elemental mapping images indicate the particles observed in Fig. 4(a) correspond to the
CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ phase, and the composition ratio of Pb:I:Cl were calculated to be 1.00:2.70:0.11 from the EDX spectrum using the Pb M$\alpha$, I L$\alpha$ and Cl K$\alpha$ lines with background correction by normalizing the spectrum peaks on the atomic concentration of Pb element. This result indicates that I might be deficient from the starting composition of CH$_3$NH$_3$PbI$_{2.88}$Cl$_{0.12}$, and the deficient I might increase the hole concentration. 

The CH$_3$NH$_3$PbI$_3$ crystals have perovskite structures, and provide structural transitions from tetragonal to cubic system upon heating at $\sim$330 K, as shown in the structure models of Figs. 3(c) and 3(d). For the highest temperature phase, both the CH$_3$NH$_3$ ions and iodine (I) ions are disordered, which results in disordered cubic phase, as shown in Fig. 3(c). Site occupancies were set as 1/4 for I in the structure model. As the temperature lowers, the cubic phase was transformed into the tetragonal phase, and I ions are ordered, which results in the lower symmetry of tetragonal from the cubic symmetry, as shown in Fig. 3(d). For the high temperature phase, unit cell volume of the cubic structure is 261.0 Å$^3$, which is bigger than that of the tetragonal structure (245.6 Å$^3$), as listed in Table 2. This would be due to both thermal expansion of the unit cell and atomic disordering of I in the cubic phase.

The XRD results in Fig. 3 indicated phase transformation of the CH$_3$NH$_3$PbI$_3$ perovskite structure from tetragonal to cubic system by partial separation of PbI$_2$ from CH$_3$NH$_3$PbI$_3$ phase.
result in the increase of the efficiency in the present work is due to the partial separation of PbI₂ that the structure transition from the tetragonal to cubic structure, which might also reduce the cell volume. It should be noted that the SEM-EDX result, site occupancies of I atom would be less than PbI₂.92Cl0.08 cells.

The perovskite CH₃NH₃PbI₃ phase shows photo-conversion efficiencies between 300 and 800 nm, which almost agrees with reported energy gaps of 1.51 eV and 1.61 eV (corresponding to 821 and 770 nm, respectively) for the CH₃NH₃PbI₃ phase. This indicates that excitons and free charges would be effectively generated in the perovskite layers upon illumination by visible light. In the present work, the energy gap of the CH₃NH₃PbI₃ phase increased from 1.578 to 1.590 eV by Cl-doping, as listed in Table 2, which could contribute the increase of open-circuit voltage. IQE spectra of TiO₂/CH₃NH₃PbI₃ and TiO₂/CH₃NH₃-PbI₂.92Cl0.08 were calculated from the EQE and transmittance, as shown in Fig. 5(b). The IQE of both cells increased in the range of 500–800 nm, which indicates that increase of the light absorption in the range of 500–800 nm would increase the conversion efficiencies of the TiO₂/CH₃NH₃PbI₃ Cl/spiro-OMeTAD cells.

An energy level diagram of TiO₂/CH₃NH₃PbI₃–Cl[sub x] photo-voltaic cells is summarized as shown in Fig. 6. Previously reported values were also used for the energy levels of the figures by adjusting them to the present work. An energy barrier would exist at the semiconductor metal interface. The electronic charge generation is caused by light irradiation from the FTO substrate side. The TiO₂ layer receives the electrons from the CH₃NH₃PbI₃ crystal, and the electrons are transported to the FTO. The holes are transported to an Au electrode through spiro-OMeTAD. Experimental evidence for photogenerated free carriers, which would enhance the carrier transport, was reported. In the present work, the samples were prepared in air, which may result in the reduction of the photo- and thermal stability. Perovskite crystals with higher quality should be prepared in further works.

4. Summary

In conclusion, TiO₂/CH₃NH₃PbI₃–Cl[sub x]-based photovoltaic devices were fabricated by a spin-coating method using a mixture solution, and effects of PbCl₂ addition to the perovskite CH₃NH₃PbI₃ precursor solutions on the photovoltaic properties were investigated. The microstructures of the devices were investigated by XRD and SEM, which indicated phase transformation of the perovskite structure from cubic to tetragonal system by heavy Cl-doping to the CH₃NH₃PbI₃ phase. A small amount of Cl-doping (CH₃NH₃PbI₃–Cl[sub x]) at the I sites improved the efficiencies to ~8%, which would be due to preservation of the cubic structure and expansion of energy gap and diffusion length of excitons. Both IQE and EQE were improved in the range of 300–800 nm by the small amount of Cl-doping, and the IQE results indicates that the suppression of the reflection in the range of 500–800 nm would improve the efficiencies further.

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