Extended Abstracts of the 2017 International Conference on Solid State Devices and Materials, Sendai, 2017, pp1089-1090

PS-15-06

Investigation of Thermal Treatment Effects of PbI_2 Film Yielded Two-step Type Perovskite Solar Cells

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Abstract

A precise control of the morphology and crystallization of perovskite thin-films is well-correlated to higher perovskite solar cells performances. The methylamonium lead iodide ($MAPbI_3$) film is fabricated by intercalating of MAI molecules into PbI_2 film. Hence, crystal growth control of PbI_2 is important to obtain highly efficient perovskite film. Herein, we attempt to control the crystal growth of PbI_2 through a simple spin-coating method via varying annealing temperature of 70, 150, and 250 °C for 1, 5, 10, and 30 min. We also investigate the effect of PbI_2 crystallinity on the performance of resulting perovskite solar cells.

1. Introduction

Organometallic halide perovskite (PSCs) have recently emerged as promising cost-effective and highly efficient nanostructured solar cells[1, 2)]. The first PSC with a power conversion efficiency (PCE) of 3.81% was reported in 2009 by Kojima *et al*[3)]. Currently, typical PCE values of perovskite solar cells are over 20%[1)] far higher than that of organic thin-film solar cells. In the formation of $MAPbI_3$ (methylamonium lead iodide, $CH_3NH_3PbI_3$) perovskite crystal, it is considered that MAI (methylammonium iodide, CH_3NH_3I) intercalates into PbI_2 film as shown in **Fig. 1**. However, it is not cleared that the relationship of the film quality and crystallinity of the PbI_2 film with influence of MAI intercalation by using two-step method.

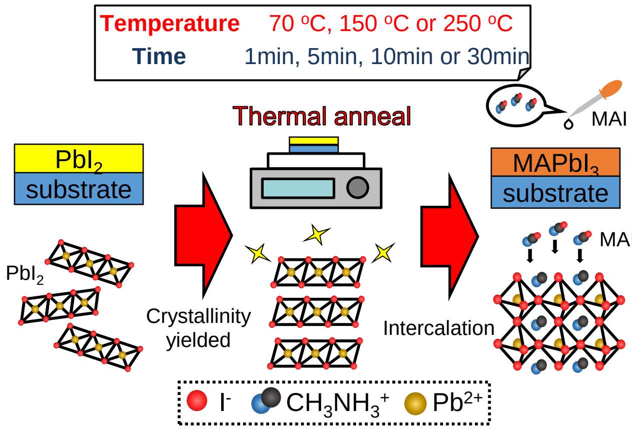

Fig. 1. Schematic illustration of formation mechanism of PbI_2 and $MAPbI_3$ film affected by thermal annealing.

The PbI_2 assumes different crystal phases depending on temperature; therefore it is considered that the crystallinity, morphology and the like of the PbI_2 film change by thermal annealing.

In this study, we aimed to elucidate the control of PbI_2 crystal growth for precise intercalation to yield efficient, perovskite thin-film and solar cells.

2. Experiment

Device structure of our PSCs is ITO / compact-TiO_2 / $MAPbI_3$ / spiro-OMeTAD / Ag. Bare ITO was treated with oxygen plasma for 20 min before use. The compact-TiO_2 layer was prepared by chemical bath deposition (CBD) method[5)]. The perovskite layer was formed by sequential solution deposition and spin-soating of PbI_2 and MAI. $MAPbI_3$ was formed using two-step spin-coating procedure. PbI_2 solution was prepared by dissolving 230 mg PbI_2 in 1 ml N, N-dimethylformamide (DMF, 99.5%, Kanto Chemical) under stirring at room temperature (RT). PbI_2 solution (100 μl) was spin-coated on the compact-TiO_2 film at 2,000 rpm. for 30 s without loading time. After spinning, the film was dried at 70 °C, 150 or 250 °C for 1, 5, 10 or 30 min and after cooling to RT, MAI solution (0.063 M, 10mg/ml) in 2-propanol was loaded on the PbI_2 coated substrate for 10 s as loading time, which was spun at 2,000 rpm. for 30 s and dried at 70°C for 5 min and 100 °C for 10 min, and 120 °C for 10 min. Finally, we obtained 200 nm-thick $MAPbI_3$ film. Then, hole transport layer (spiro-OMeTAD) and Ag electrode were deposited in glove box and evaporation chamber without air expose, respectively. X-ray diffraction (XRD) patterns of the prepared films were measured using an X-ray diffractometer (SmartLab, Rigaku, Japan) with an X-ray tube (Cu Kα, λ= 1.5406 Å). Ultraviolet-visible (UV-Vis) absorption spectra of perovskite films were measured using an absorption spectrophotometer.

3. Results

In terms of addressing the structural properties (e.g. full-width at half maximum, FWHM) of PbI_2 and $MAPbI_3$ films, we applied X-ray diffraction (XRD). The lower FWHM has a relationship with higher crystallinity of film. In case of annealing temperature of PbI_2 film for 1 min, the FWHM of PbI_2 yielded $MAPbI_3$ film was reduced by higher annealing temperature, as shown in **Fig. 2.**

The PbI_2 and $MAPbI_3$ films morphology were analyzed with scanning electron microscopy (SEM) as shown in **Fig.**

3. The images in **Fig. 3(d)-3(f)** reveal that while increasing the annealing time and temperatures increases the crystallinity of PbI_2, leading to the large grain size of resulting PbI_2 yielded $MAPbI_3$ thin-films. In contrast, lower annealing temperature conditions have remained extra MAI (red circle) as shown in **Fig. 3(d) and 3(e)** on the resulting MAPbI3 thin-film. These results suggest that high crystallinity PbI_2 allow the perfect intercalation of MAI molecules, compared to low crystallinity PbI_2 film.

As can be revealed that in terms of annealing time of PbI_2 film at 250 °C, the crystallinity was remained the same. In contrast, the UV-vis spectrum of $MAPbI_3$ film were found to increase absorption depending on annealing time of PbI_2 film at 250 °C as shown in **Fig. 4.**

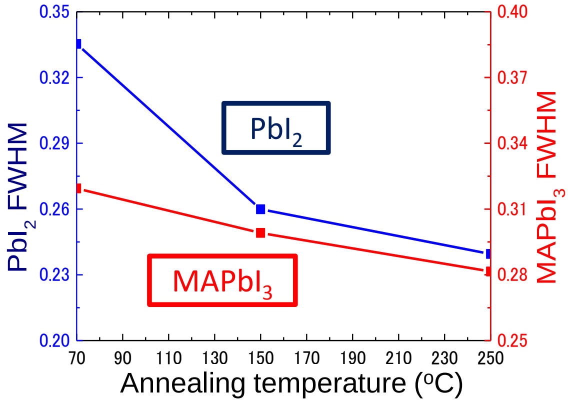

Fig. 2. The FWHM of PbI_2 diffraction peak (001) and $MAPbI_3$ diffraction peak (110) calculated by XRD spectrum depending on annealing temperature of PbI_2 film for 1 min.

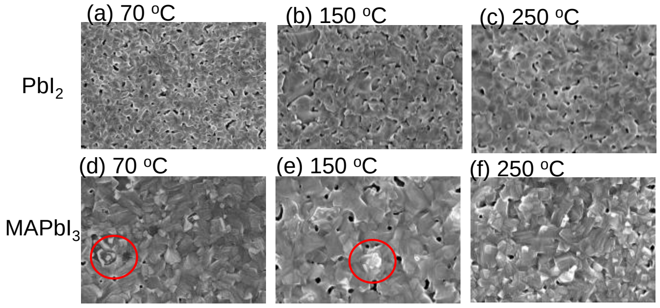

Fig. 3. The SEM images of PbI_2 film surface annealed by (a)70 °C, (b) 150 °C and (c) 250 °C. The $MAPbI_3$ surface using PbI_2 annealed by (d) 70 °C, (e) 150 °C and (f) 250 °C.

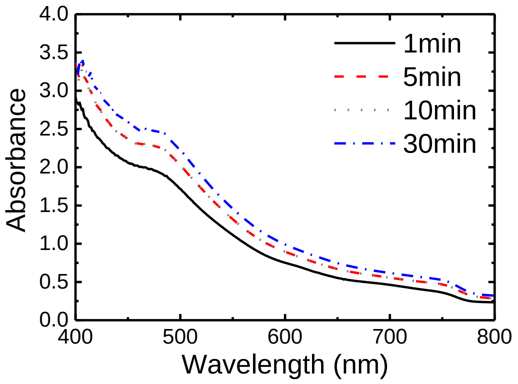

Fig. 4. The UV-vis spectrum of $MAPbI_3$ film depending on annealing time of PbI_2 film at 250 °C.

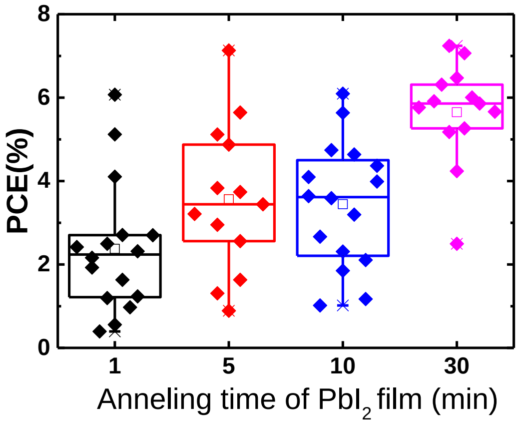

Fig. 5. Reproducibility results of perovskite solar cells in term of PbI_2 film annealing time at 250 °C.

Optimum annealing temperature was found at 250 °C for the resulting devices fabrication. Power conversion efficiencies (PCEs) were increased considerably in the average range of 2.38±1.52% to 5.65±1.18%, while improving the annealing time of 1 to 30 min as shown in **Fig. 5**. The best control and highest reproducibility was observed for the control PbI_2 crystal film annealed with 30 min, leading to an enhanced charge dissociation and transport efficiency and reduction in recombination events in the solar cells. This highlights that the crystallinity of PbI_2 significantly affected to the resulting of $MAPbI_3$ solar cell performance.

4. Conclusions

We investigated the effect of crystallinity of PbI_2 on the performance of resulting $MAPbI_3$ solar cells. The crystallinity of PbI_2 yielded $MAPbI_3$ film was increased by higher annealing temperature. PCEs were increased considerably in the average range of 2.38±1.52% to 5.65±1.18%, while improving the annealing time of 1 to 30 min. Our results suggested that the crystallinity of PbI_2 significantly affected to the resulting of $MAPbI_3$ solar cell performance.

Acknowledgements

This research work was partially supported by research grant from Japan Power Academy, Research Grant of Tateishi Science and Technology Foundation, 2017 Research Grant of Iketani Science and Technology Foundation, 2016 Research Grant of Iwatani Naoji Fundation, 2015 Basic Research Grant of TEPCO Memorial Foundation, 35th Research Grand of Tonen General Sekiyu Foundation, and JSPS KAKENHI Grant 16K05882.

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