Conversion of metal-organic halide perovskite from PbI_2 precursor films grown by hot-wall method

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Abstract. We report on metal-organic halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ films converted from PbI_2 precursors for planar heterojunction perovskite solar cells. PbI_2 films as a precursor were deposited by hot-wall method and conventional vacuum evaporation. The conversion to perovskite phase from the PbI_2 films were performed by annealing in methyl ammonium iodine (MAI) vapour at 120-150 °C. We confirmed that no residual PbI_2 phase can be detected in the converted perovskite films by x-ray diffraction measurements. The surface morphology of the perovskite films was measured by AFM. Roughness R_a of the films is 17.8 nm, which is comparable value to the reported ones. Using the converted perovskite films we fabricated tentative perovskite solar cells with a device architecture of ITO/PEDOT:PSS/Perovskite/ C_{60} /Ag. The power conversion efficiencies of the fabricated solar cells from a conventional evaporation and the hot-wall method exhibited 2.22 and 2.33%, respectively.

1 INTRODUCTION

Metal-organic hybrid perovskite solar cells have been extensively studied by many researchers all over the world and its power conversion efficiency (PCE) reaches over 20%, recently [1-3]. The fabrication methods of perovskite film are classified mainly into two method: one is a solution growth method from precursor solutions of PbI_2 and MAI or their mixed solution by a spin-coating technique, and another is a vapour growth method by conversion of perovskite phase from PbI_2 films by annealing under methyl ammonium iodide (MAI) vapour. The PbI_2 films as precursor are deposited by a spin-coating or a conventional vacuum evaporation. These perovskite films have been deposited on porous TiO_2 scaffolds. Recently, perovskite solar cells with flat substrates such as compact TiO_2 [4], PEDOT:PSS/ITO [5, 6] have extensively been studied. The perovskite solar cells using these flat substrates possess planar heterojunctions. In planar heterojunction perovskite solar cells, the qualities of perovskite film itself such as surface morphology (roughness and pin-hole free) and crystallinity is key factors to fabricate high-efficiency perovskite solar cells. It is also reported that the crystallinity of PbI_2 as a precursor affects the film quality of converted perovskite layer by thermal annealing under a MAI vapour atmosphere [7]. PbI_2 films deposited from vapour phase are usually used by a conventional vacuum evaporation. On the other hand, the hot-wall method is known as a high-quality deposition technique for inorganic and organic semiconductor films [8-11]. The hot-wall method is one of the vapour deposition techniques and can be deposited under a quasi-thermal equilibrium condition [12]. The

deposited films are therefore high quality, compared to those by a conventional evaporation technique.

In this paper, we have studied conversions of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films from PbI_2 films deposited by the hot-wall method as well as a conventional evaporation method. We compared crystalline quality of the converted perovskite films by x-ray diffraction and surface morphology by atomic force microscope (AFM). In addition, we have tentatively fabricated perovskite solar cells using the converted perovskite films from PbI_2 deposited by the hot-wall method. The fabricated perovskite solar cells were measured current-density voltage characteristics under an AM1.5G light irradiation using a solar simulator.

2 Experimental

Perovskite films were fabricated by a conversion from PbI_2 film by an annealing under a MAI vapour at 120-150 °C. The PbI_2 films were deposited by two kinds of method: a conventional vacuum evaporation and a hot-wall method. The hot-wall evaporation system equipped with a hot-wall furnace was a home made one. The hot-wall furnace installed into a vacuum chamber is shown in Fig. 1. The quartz tube is surrounded by three zones with separated heaters. Each zone consists of wall zone, source zone and reservoir zone. Their temperatures were controlled independently by PID temperature controllers. PbI_2 source materials (99.99%) are placed in the source zone of a quartz tube. The reservoir zone was not used in this study. The substrate temperature was kept at 100 °C during deposition of PbI_2 film by the hot-wall method. In the case of the depositions of PbI_2 films by a conventional vacuum evaporation, on the other hand, no

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substrate heating was performed. The source and wall temperatures are 200 and 180 °C, respectively. The base pressure of the vacuum chamber is less than 5×10^{-6} Torr.

Fig. 1. Hot-wall furnace in a vacuum chamber.

The device structure and band diagram of perovskite solar cells are shown in Fig. 2. The device architecture as shown in Fig. 2(a) is the so-called inverted planar heterostructure: ITO/PEDOT:PSS/Perovskite/C60/Ag. PEDOT:PSS film was spin-coated on patterned ITO glass followed by annealed for 30 min at 150 °C. C60 and Ag films were deposited by a conventional vacuum evaporation. It is pointed out here that the sample transfers from one process to a subsequent process were performed in an ambient atmosphere with humidity. On the other hand, the reported perovskite films in solar cells with high PCEs were fabricated in a glove box without oxygen and water vapour.

Surface morphology of the perovskite films was observed by an atomic force microscope (AFM). Crystalline phase of the converted perovskite films was confirmed by x-ray diffraction (XRD) measurements. Current density-voltage characteristics was measured with a source meter (Keithley 2612B) under AM1.5G light irradiation using a solar simulator.

Fig. 2. The device architecture (left) and energy diagram (right) of the fabricated planar heterojunction solar cells.

3 Results and discussion

Figure 3 shows morphologies of the converted perovskite films from PbI_2 precursor deposited by a conventional evaporation (left) and the hot-wall method (right). The arithmetical mean roughness R_a of the films are 19.3 and 17.8 nm, respectively. Although, the perovskite film converted from PbI_2 deposited by a vacuum evaporation exhibits uniform surface, the roughness is still high for planar heterojunction solar cells. It is noticed that flatter areas can be seen on the surface of the perovskite film converted from the hot-wall method. This result shows that the hot-wall method is a potential method to fabricate flatter perovskite film compared to a vacuum evaporation. We believe that more flat perovskite films for planar heterojunction solar cells can be achieved by adjusting the growth condition like deposition rate and substrate temperature.

Fig. 3. AFM images ($5 \times 5 \mu\text{m}$) of the perovskite films converted from PbI_2 films deposited by a conventional vacuum evaporation (left) and a hot-wall method (right).

In order to confirm a perovskite phase of the converted films from PbI_2 precursor by the thermal annealing under a MAI vapour, we measured XRD. The measured XRD patterns are shown in Fig. 4. Both of the XRD patterns of the converted perovskite films shows relatively strong XRD peaks at 14.1° , 24.5° , 28.4° , 31.9° and 43.2° exhibiting (110), (211), (220), (310) and (330) planes from a perovskite phase, respectively. No additional XRD peaks related to PbI_2 phase (e.g. 12.7°) can be seen in the converted perovskite films in Fig. 4. This implies that the PbI_2 films as precursor converted completely to a perovskite phase by the thermal annealing under MAI vapour. Furthermore, high intensity peaks from (110) and (220) planes indicates that the converted perovskite films are highly oriented with respect to the substrate.

Fig. 4. X-ray diffraction patterns of the converted perovskite films from PbI_2 precursor deposited by a conventional vacuum evaporation and hot-wall method. X-ray diffraction pattern of a bare PbI_2 film is also shown.

Finally, we fabricated planar heterojunction perovskite solar cells by using the converted perovskite films discussed above. We named here each solar cell #1 and #2. The solar cell #1 is a solar cell fabricated from PbI_2 precursor deposited by a conventional vacuum evaporation, the solar cell #2 is a solar cell fabricated from the hot-wall method. The current density-voltage (J - V) characteristics is shown in Fig. 5, and the device performance parameters, short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and PCE are summarized in Table 1. Although the J - V characteristics of the fabricated perovskite solar cells vary from sample to sample in this study, no significant differences can be found in the two kinds of solar cells, as can be seen in Fig. 5. The J_{sc} of the perovskite solar cell #1 is slightly higher than the solar cell #2. On the contrary, the V_{oc} shows higher value in the solar cell #2, which was fabricated from the hot-wall deposited PbI_2 precursor film, than solar cell #1, which was fabricated from a vacuum evaporated one. The cell performance parameters FF and PCE of two solar cell #1 and #2 are comparable. However, these performance parameters is considerably lower than the reported ones. We think that the main reasons of the low performances are most probably due to a fabrication process under an ambient environment with humidity, pin-holes in the perovskite film and flatness of the film. Several researchers reported efficient perovskite solar cells prepared in ambient air with humidity [13, 14]. Therefore we expect that high efficient perovskite solar cells could also be fabricated by our process. However, pin-holes and flatness of perovskite film is serious issues to achieve higher performance of planar perovskite solar cells. In particular, low FF is caused mainly by low shunt resistance arising from pin-holes in perovskite film. As mentioned before, the perovskite film prepared by the hot-wall deposited PbI_2 precursor has flatter surface. If

the flatter surface expanded to an entire surface, the pin-holes could significantly be reduced. Further experiments using the hot-wall method are needed to achieve the depositions of high quality flat perovskite films by optimizing the growth and anneal conditions of PbI_2 films.

Fig. 5. Current density-voltage characteristics of the perovskite solar cells fabricated by two kinds of converted perovskite films.

Table 1. Performance parameters of fabricated planar heterojunction solar cells.

Solar cell	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
#1	5.82	0.822	0.463	2.22
#2	5.60	0.873	0.479	2.33

4 Summary

We developed a method to convert PbI_2 precursor films into perovskite phase. The PbI_2 films were prepared with two kinds of deposition method: a conventional evaporation and the hot wall method. The conversion of PbI_2 films into perovskite phase was completed by a thermal annealing under MAI vapour. We fabricated solar cells with a planar heterojunctions using these perovskite films. The PCE was as low as 2.33%. We speculated that the low PCEs were mainly due to pin-holes and flatness in the perovskite films. We found that the hot-wall method for PbI_2 precursor film was a potential method to fabricate pin-hole free and flat perovskite films.

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