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Modified solvent bathing method for forming high quality perovskite films

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ABSTRACT

We developed a new perovskite film forming process based on solvent bathing method. The preheating of substrate before spin-coating of precursor solution drastically changed the quality of the obtained perovskite films. The perovskite films formed by modified solvent bathing method were much dense with large grains. The improvement of open circuit voltage implied that the modification succeeded to form the better interface between TiO_2 and perovskite layer and to grow the higher quality perovskite layer. Finally, we obtained the best conversion efficiency of 12.6%. Although the conversion efficiency of this work is not sufficient compared with other reports, our modified solvent bathing method has a wider process window comparing to the commonly used anti-solvent dipping methods. We expect that our modified method can also applied to monolithic tandem solar cells.

1. Introduction

The perovskite solar cell based on organometal halides such as $CH_3NH_3PbI_3$ ($MAPbI_3$) is a new class of solar cell which has been found to have a high potential as solar cell material by Miyasaka's group in 2009 [1]. Since two different groups reported a conversion efficiency of nearly 10% in 2012 [2, 3], research on perovskite solar cells exploded and spread rapidly all over the world. Currently there are many reports that conversion efficiency exceed 20% [4–8]. Such a high conversion efficiency is exhibited by organometal halides perovskite having very excellent properties as a solar cell material as shown below; excellent light absorption characteristics [9, 10], small exciton binding energy [11, 12], long carrier diffusion length [13, 14], high carrier mobility [15, 16].

In addition, the film formation method of the perovskite thin film has been examined and developed from the most general spin-coating method, including a sequential deposition method [17], a vacuum co-evaporation method [18], and a vapor-assisted solution process [19]. In particular, a very wide variety of solvent engineering technique have been proposed for the spin-coating method [20–24]. Among them, the most commonly accepted method at the present time is a technique called a anti-solvent method [20, 21]. The anti-solvent method is a method of dropping anti-solvent such as toluene or chlorobenzene while spin-coating of a perovskite precursor solution in *N,N* -dimethylformamide (DMF) or dimethyl sulfoxide (DMSO) as a solvent. When an anti-solvent is dropped onto the film of the perovskite precursor, solvent substitution occurs quickly, and a perovskite thin film is formed immediately. The perovskite thin film prepared by this method is a homogeneous and dense high quality thin film, and many of the currently reported high efficiency solar cells use this method [25–27]. However, a challenge for this method is the very narrow time window for adding the anti-solvent, which makes it a difficult transition to any of the mentioned scalable methods.

Therefore, a solvent bathing (SB) method has been proposed as one of different solvent engineering approaches [22, 28]. The room-temperature solvent substitution concept is used for the deposition of perovskite films. The perovskite precursor solution is spin-coated onto the substrate, and immersed into a bath of anti-solvent at room temperature. Instead of heating by dropping an anti-solvent, immersing into a bath of anti-solvent realizes uniform and rapid solvent substitution. This results in efficient solvent substitution and induces rapid crystallization of uniform, ultra-smooth perovskite thin films. We focused that this method is an effective perovskite film forming method which is very suitable for mass production from the viewpoint that the process window is wide. Furthermore, since this process is a very mild film forming method, it can be expected for application to tandem solar cells [29–33]. In this work, we found that preheating before spin-coating in the bathing method drastically improves the quality of the perovskite film to be formed and improves conversion efficiency.

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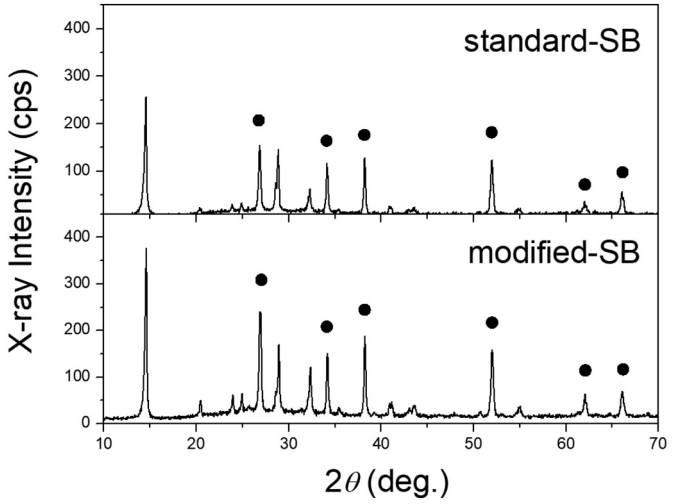

Fig. 1. XRD patterns of the perovskite thin films formed by standard SB method (upper) and modified SB method (lower). The black circle symbols in the figure correspond to the XRD peaks derived from the perovskite structure.

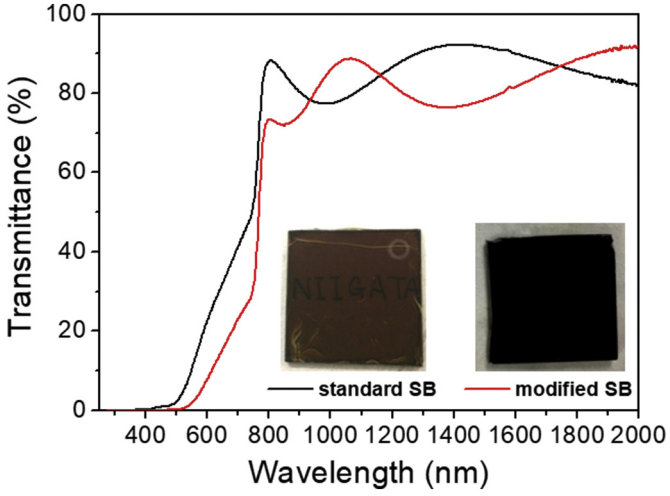

Fig. 3. The transmittance spectra of the perovskite films deposited on glass by different SB methods. Inset shows photos of obtained perovskite films, respectively.

2. Experimental methods

2.1. Perovskite film fabrication

All reagent grade chemicals were obtained commercially from Wako Pure Chemical Industries unless noted otherwise. An equimolar mixture of PbI_2 (Tokyo Chemical Industry, for perovskite precursor [34]) and methylammonium iodide (MAI) was dissolved in *N*-methyl-2-pyrrolidone (NMP) at room temperature. The previously TiO_2-deposited fluorine-doped tin oxide (FTO) coated glass substrates (Furuuchi Chemical Corporation) was preheated on a hotplate at several temperatures (80, 100, or 120 °C). The prepared perovskite precursor solution was spin-coated onto the preheated substrates at several rotational speeds (4500, 5500, or 6500 rpm) for 15 s. In the standard SB method, spin-coating was carried out at room temperature at a rotation speed of 4500 rpm for 15 s. Immediately after spin-coating, the substrates were dipped into a 30 ml of anhydrous diethyl ether (DEE) bath and kept immersed until a brown film formed in 2 min. The fabricated perovskite films were dried at room temperature. The entire perovskite film fabrication process was performed in an inert glovebox.

2.2. Solar cell fabrication

The FTO glass (2 cm × 2 cm) were ultrasonically cleaned with acetone, methanol, and deionized water, sequentially, and then were blow-dried in nitrogen. Before deposition of other films, the FTO

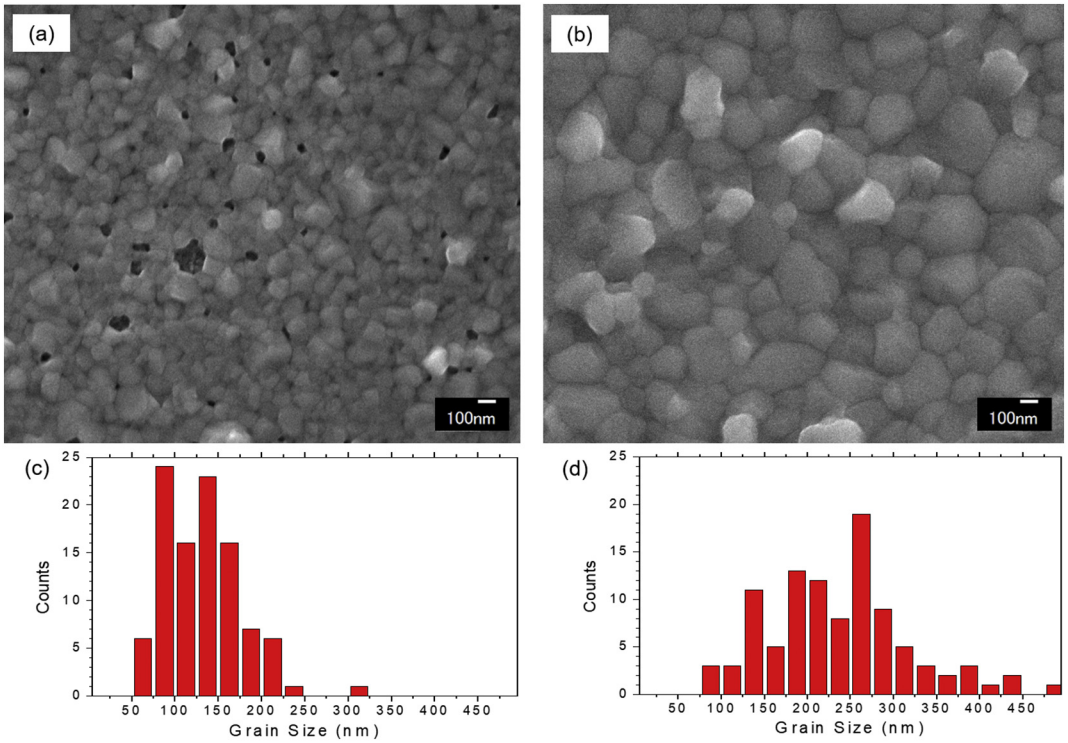

Fig. 2. The SEM images of surface morphology of the perovskite thin films formed by standard SB method (a) and modified SB method (b). The grain size distributions are shown for (c) and (d), respectively.