Research Paper

Fabrication of MASnI_3 and $\text{MASn}_x\text{Pb}_{(1-x)}\text{I}_3$ Thin Films by Conversion from SnS Thin Film

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Abstract

Methylammonium lead halide (MAPbI_3), an organic-inorganic hybrid perovskite material, is promising as light absorbing materials of solar cells. Nevertheless, necessity of reducing Pb contents in the perovskite materials is increasing due to the toxicity of Pb. Recently, tin-lead mixed perovskite materials have been studied intensively, by dissolving Sn and Pb sources simultaneously in one precursor solution. Here, for the first time, we report a two-step method to synthesize MASnI_3 and $\text{MASn}_x\text{Pb}_{(1-x)}\text{I}_3$ films. The films were prepared via spin-coating MAI or MAPbI_3 precursors on as-prepared SnS thin films. Crystal structures, phases, surface chemical states, and morphologies of the MASnI_3 and $\text{MASn}_x\text{Pb}_{(1-x)}\text{I}_3$ films were investigated. Our two-step method is expected to be used not only for Sn based perovskites but also for diverse compositions of perovskite materials.

Keywords: Organic-inorganic hybrid perovskite, MASnI_3 , $\text{MASn}_x\text{Pb}_{1-x}\text{I}_3$, SnS, Thin film

1. Introduction

Organic-inorganic hybrid perovskite materials have been attracting great attention due to superior photovoltaic properties, such as long carrier diffusion length, high absorption coefficient and tunable bandgap, and to low cost and low process temperature [1-6]. Especially, lead (Pb) based perovskite materials (APbX_3 , A = methylammonium (MA), formamidinium (FA) or Cs, and X = Cl, Br or I) have been researched as photodetectors [7,8], light-emitting diodes [9,10], lasers [11] and perovskite solar cells (PSCs) [1,12]. PSCs based on Pb containing perovskite materials have been rapidly developed from 3.8 % of power conversion efficiency (PCE) at 2009 [13] to over than 23 % recently [14]. However, there was always a big issue regarding harmfulness of Pb, so the lead-free perovskite materials have been drawn interests. Tin (Sn) based perovskite light absorbing materials have been one of the promising alternatives because of the lower bandgap up to the NIR range and less toxicity [15-17]. Besides, they have been studied for the tandem solar cells to achieve high efficiency because of their wide range light absorption [18]. Nevertheless, perovskite composition incorporating only Sn had some limitations that high carrier concentration

and mobility, due to behave like conductors, so it is known that not suitable for PSCs [17]. Furthermore, under the ambient condition, the Sn^{2+} oxidizes to more stable Sn^{4+} , leading to more metallic [15,16] and decomposition of ABX_3 perovskite structures. To overcome these problems, Kanatzidis et al. introduced Sn-Pb mixed perovskite compositions [15]. When Pb was added to MASnI_3 , electrical properties and the amount of Sn^{4+} were controlled and made it possible to operate the PSCs better. Also, it enabled bandgap tuning and band alignment modification in accordance with the ratio of Pb to Sn. Moreover, Hayase et al. reported that incorporation of Ge into Sn-perovskite increases PCE and the stability in the ambient condition of PSCs [19]. However, in most cases, Sn-Pb mixed perovskite thin films were synthesized by one-step spin-coating of a precursor dissolving the Sn halide and Pb

Figure 1. Band alignment of electrode, electron transport materials (TiO_2 , PCBM), hole transport materials (HTM), $\text{MASn}_x\text{Pb}_{(1-x)}\text{I}_3$ ($x = 0 \sim 1$), for perovskite solar cells [17].

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halide sources.

In this paper, MASnI_3 and $\text{MASn}_x\text{Pb}_{(1-x)}\text{I}_3$ thin films were synthesized, by a two-step method; spin-coating MAI or MAPbI_3 precursor on an as-prepared vapor-transport-deposited (VTD) SnS thin films. Successful synthesis of MASnI_3 and $\text{MASn}_x\text{Pb}_{(1-x)}\text{I}_3$ thin films were confirmed by structural, surface chemical and morphological analyses. We found from literatures that MASnI_3 and $\text{MASn}_x\text{Pb}_{(1-x)}\text{I}_3$ have slightly higher conduction band edges than electron transport materials (TiO_2 , [6,6] phenyl C61 butyric acid methyl ester (PCBM)) of PSCs (Fig. 1) [17,20], which would make the Sn-perovskite layers suitable for light absorption layers of PSCs. Moreover, our experimental results show SnS residue layer after the synthesis of Sn-perovskite films, implying formation of junction of $\text{MASnI}_3/\text{SnS}$ or $\text{MASn}_x\text{Pb}_{(1-x)}\text{I}_3/\text{SnS}$ which would be helpful for extracting holes to a metal electrode due to slightly higher valence band edges of SnS than that of Sn-perovskites (Fig. 1).

II. Experiments

1. SnS thin film fabrication

SnS thin films were deposited by VTD using a one-zone tube furnace (S&R Korea, SRVF-LV-3B-1508). 4N SnS source powder (iTasco, LT40SNS312) was loaded in the middle of the heating zone [Fig. 2(a)]. The process pressure was set at 1.4 Torr by flowing Ar 100 at sccm, and the process temperature was set at 530 °C. The growth duration was 15 min to obtain ~500-nm-thick SnS. Further details on the growth of SnS and its properties can be found elsewhere [21].

2. MASnI_3 thin film fabrication

MASnI_3 thin film was synthesized by spin coating MAI precursor solution on the SnS thin film at 3000 rpm for 7 s. MAI precursor was prepared by dissolving the MAI (Xi'an Polymer Light Technology Corp., $\geq 99.5\%$) powder in N,N-dimethylformamide (DMF, Sigma-Aldrich, anhydrous, 99.8 %) for 29.7 wt%. MAI coated substrates were annealed at 130 °C for 4 hr.

3. $\text{MASn}_x\text{Pb}_{(1-x)}\text{I}_3$ thin film fabrication

To make the $\text{MASn}_x\text{Pb}_{(1-x)}\text{I}_3$ thin film, MAPbI_3 precursor was spin coated on the SnS thin film at 4000 rpm for 20 s. MAI, PbI_2 (Tokyo Chemical Industry, 99.99 %), dimethyl sulfoxide (DMSO, Sigma-Aldrich, anhydrous, $\geq 99.9\%$) was mixed in DMF as molar ratio 1:1:1 for 26 wt% to prepare the MAPbI_3 precursor solution. During the spin coating, 0.5 ml of diethyl ether (Sigma-Aldrich, anhydrous, $\geq 99.7\%$) was dripped to the substrate. Then, the substrate was sequentially annealed at 65 °C for 1 min and at 130 °C for 10 min.

4. Characterizations

Crystal structure of thin films were investigated by X-ray diffraction (XRD, X'Pert PRO, PANalytical). The top-view morphology and cross-sectional structure with thickness were characterized using field-emission scanning electron microscopy (FE-SEM, JSM-6710F, JEOL). The chemical state and elemental analysis were performed by X-ray photoelectron spectroscopy (XPS, Theta Probe AR-XPS System, Thermo Fischer Scientific).

III. Results and discussion

1. SnS thin films

First, SnS thin film was synthesized on a FTO/glass substrate for structural characterization. Space group Pbnm orthorhombic SnS was identified by XRD pattern (Fig. 2(b), ICDD 039-0354) and there were no any secondary phases. Dense and pinhole-less film was formed as shown in cross-sectional SEM image [Fig. 2(c)]. Using this SnS thin films, the MASnI_3 and $\text{MASn}_x\text{Pb}_{(1-x)}\text{I}_3$ thin films were fabricated.

2. MASnI_3 thin films

MASnI_3 thin film was synthesized via the two-step method, by spin-coating the MAI solution on the SnS thin film, followed by annealing at 130 °C for 4 hr. Figure 3(a) shows XRD patterns of MAI coated SnS thin films. New peaks such as at $2\theta = 14.1^\circ$ and 24.8° are assigned to (001) and (002) crystal planes of cubic structured MASnI_3 . In addition, unreacted residual SnS is found in XRD patterns. MAI is considered to be fully used to make MASnI_3 because MAI peak is not observed at all. Cross-sectional and top-view SEM images are presented in Figs. 3(b) and 3(c). The cross-sectional image shows a dense and pinhole-free film, while top-view image shows a lot of pores with a rough surface. This implies that the reaction of MAI and SnS was started from the top of SnS and leading non-uniform film morphology.

Figure 2. (a) Schematic of SnS growth process by VTD and fabricated SnS thin film. (b) XRD pattern and (c) scanning electron microscopic (SEM) image of the synthesized SnS thin film.

Figure 3. (a) XRD pattern of MAI coated SnS thin film. (b) Cross-sectional SEM image of result thin film and (c) top-view SEM image.

3. $\text{MASn}_x\text{Pb}_{(1-x)}\text{I}_3$ thin films

The Sn-Pb mixed perovskites were synthesized via similar method using an SnS thin film; MAPbI_3 precursor solution was spin-coated on the SnS thin film with anti-solvent dripping. Figure 4(a) shows the XRD pattern of MAPbI_3 coated SnS thin film. There were several peaks corresponding to Sn-Pb mixed perovskite and SnS residue. To further investigate the phase of the Sn-Pb mixed perovskites film, the main peak around 2θ -14° is compared with those of MASnI_3 and MAPbI_3 (Fig. 4(b)). It is notable that 2θ of the main peak of MASnI_3 is larger than that of MAPbI_3 , indicating smaller lattice parameter of MASnI_3 . On the other hand, Sn-Pb mixed perovskite shows the main peak at the position between MAPbI_3 and MASnI_3 . Therefore, it can be deduced that smaller Sn ion from SnS diffuses in to the lattice of MAPbI_3 during the annealing process. The presence of PbI_2 in XRD pattern indicates that some MAI in the precursor reacts with SnS in advance to the crystallization of MAPbI_3 by reaction with PbI_2 .

XPS measurement was carried out to examine presence of Sn and S (Fig. 5) at the surface of the Sn-Pb mixed perovskite. As shown in Figs. 5(a) and 5(b), C 1s and Pb 4f binding energies are similar with previous report [22]. Also, Sn is clearly observed from the surface, as shown in Fig. 5(c). Based on the XRD and XPS results, formation of $\text{MASn}_x\text{Pb}_{(1-x)}\text{I}_3$ even in the top of the perovskite film is assured, implying diffusion of Sn ion from the bottom SnS layer to the top of the post-coated (MAI-PbI₂ mixed) layer. Sulfur is not detected as shown in Fig. 5(d). Therefore, it can be deduced that sulfur, a by-product, is evaporated out from the film or remaining at the bottom of the film, but not doped into the perovskite lattice, because of absence of S at the surface. It is more likely that S is evaporated, because we couldn't find any thin layer, which can be assigned to sulfur layer, from the cross-sectional SEM

Figure 4. (a) XRD pattern of MAPbI_3 coated SnS thin film and (b) the peak shift of perovskite main peak. (c) Cross-sectional and (d) top-view SEM image of synthesized thin film.

Figure 5. XPS patterns Sn-Pb mixed perovskite synthesized from MAPbI_3 coated SnS thin film. (a) C 1s, (b) Pb 4f, (c) Sn 3d, (d) S 2p.

images [Figs. 3(c) and 4(d)]. The morphology of mixed perovskite layer is shown in Figs. 4(c) and 4(d). Pinhole or pore is not observed. The film has a dense and smooth surface with ~ 200 nm sized grains, and uniform thickness, which is comparable to film quality of MAPbI_3 thin film.

IV. Summary

MASnI_3 and $\text{MASn}_x\text{Pb}_{(1-x)}\text{I}_3$ thin films were synthesized via the two-step method by spin-coating MAI or MAPbI_3 precursor solutions on SnS thin films. Based on the peak shift of XRD patterns and the presence of tin on XPS analysis, the synthesis of $\text{MASn}_x\text{Pb}_{(1-x)}\text{I}_3$ is demonstrated. The final morphology of MASnI_3 and $\text{MASn}_x\text{Pb}_{(1-x)}\text{I}_3$ was identified using SEM measurement. MASnI_3 thin film shows a rough surface with pores, while $\text{MASn}_x\text{Pb}_{(1-x)}\text{I}_3$ thin film shows a uniform, smooth and dense morphology, indicating successful synthesis of good quality $\text{MASn}_x\text{Pb}_{(1-x)}\text{I}_3$

thin film. Our two-step method is expected to be used not only for Sn-based perovskites but also for diverse compositions of perovskite materials.

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