Effect of Antisolvent Application Volume on $\text{CH}_3\text{NH}_3\text{PbI}_3$ Films

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ABSTRACT

Antisolvent treatment methods used to manufacture high-quality perovskite films using solution processes vary in terms of the type of antisolvent and processing condition employed. We analyzed the structural dependences of a perovskite film in terms of the applied volume of ethyl acetate as an antisolvent and the optical properties resulting therefrom. The application of an excessive volume of the antisolvent caused excessive pinholes in the entire area of the perovskite film. In addition, the pinholes were found to hinder the transport of charge carriers.

Keywords: Perovskite, Antisolvent, Ethyl acetate, Photoluminescence, Pinholes

1. Introduction

Organic-inorganic halide perovskites have been extensively studied for applications such as light-emitting diodes, photodetectors, and laser diodes owing to their superior optoelectrical properties such as low exciton binding energy, high absorption coefficient, and high charge carrier mobility [1–5]. In particular, they are leading the next-generation solar cell market, with the power conversion efficiency exceeding 25% [6]. Most of the high-efficiency perovskite solar cells are manufactured using an antisolvent treatment method by solution process; however, the results vary not only in terms of the type of antisolvent used, such as diethyl ether, chlorobenzene, and toluene, but also in terms of the processing condition employed (volume and time) [7–9]. In our previous study, we applied ethyl acetate (EA) as an antisolvent and demonstrated that it was the most suitable antisolvent for forming a compact perovskite film without pinholes in the ambient condition and with high reproducibility, while enabling a three times higher power conversion efficiency compared to when diethyl ether was used [10].

Based on these results, in this study, we investigated the structural and optical properties of a perovskite film in terms of the applied volume of EA as the antisolvent. Excessive use of the antisolvent caused unnecessary dissolution of the perovskite precursor material, which collapsed the perovskite film structure and increased the carrier lifetime. This could hinder the charge transport inside the perovskite film and between the adjacent charge transport layers, thereby impairing the device performance in solar cell devices.

2. Experimental details

Tin-doped indium oxide (ITO) substrates (8 Ω /sq, AMG) were sequentially and ultrasonically cleaned with isopropyl alcohol (10 min) and acetone (10 min), and the cleaned substrates were exposed to ultraviolet (UV)-ozone for 15 min. For the preparation of the electron transport layer, 15 wt.% SnO_2 aqueous dispersion (Alfa-Aesar) was diluted in the same weight ratio as deionized water. The diluted dispersion was spin-coated at 5000 rpm for 30 s and then annealed on a

hot plate at 150°C for 30 min. Before depositing the perovskite solution, the SnO_2 layer was treated with UV-ozone for 15 min.

For the $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃) perovskite precursor solution, we used the same process as previously reported [10]. Briefly, a 1.49 M MAPbI₃ precursor solution was spin-coated on a SnO_2 layer at 4,000 rpm for 30 s, and EA of different volumes was applied 8 s after the program started. The antisolvent was applied at the same dispensing rate using an automatic dispensing pipette (E3, Eppendorf) for a reliable quality of the fabricated perovskite film. To calculate the application time based on the volume of EA used in the experiment, the time for completely dispensing 5 mL of EA at the same speed was measured 10 times, and the average value was obtained by dividing with the volume used. The dispensing times based on the calculated volumes were 0.15 (100 μL), 0.45 (300 μL), 0.75 (500 μL), and 1.05 s (700 μL). After the program was finished, the product was annealed at 100°C for 2 min. All spin coating processes were performed in an ambient atmosphere (room temperature $\sim 20^\circ\text{C}$, relative humidity $\sim 40\%$).

A morphological analysis was conducted using a field emission scanning electron microscope (FESEM; S-4800, Hitachi). To analyze the optical properties of the perovskite film, the photoluminescence (PL) signal was collected with a Si photodetector using a lock-in amplifier (SR510, Stanford Research System), and a 532 nm diode-pumped solid-state laser (Changchun New Industries Optoelectronics Tech.) was used as the excitation light source. Time-resolved PL (TRPL) was measured using a FLS 920 fluorescence spectrometer (Edinburgh Instruments) and a 656 nm picosecond pulsed diode laser (EPL-655, Edinburgh Instruments).

3. Results and discussion

Figure 1 shows the FESEM images of the perovskite films as a function of the applied antisolvent volume. With increasing volume of the antisolvent, the grain size of the perovskite film gradually decreases to 206 ± 65 (100 μL), 131 ± 42 (300 μL), and 112 ± 31 nm (500 μL). On the other hand, for the 700 μL sample, we could not clearly measure the change in the grain size due to the crushing of the grain structure. As shown in Figs. 1(c) and 1(d), many pinholes exist not only

Figure 1. Top-view (a-d) and cross-sectional view (e-h) FESEM images of perovskite films as a function of the applied antisolvent volume. Scale bars correspond to 1 μm (a-d) and 500 nm (e-h).

on the surface of the perovskite but also inside the film and at the interface between the SnO_2 layers [Figs. 1(g) and 1(h)]. The presence of these pinholes means the existence of defects that act as nonradiative recombination centers, causing unnecessary recombination of the excitons in the perovskite film [11, 12]. In particular, pinholes generated at the SnO_2 junction may deteriorate the interface characteristics between the perovskite film and the electron transport layer, making it difficult to transport the photogenerated electrons to the electrode and thus deteriorating the device characteristics [13]. However, as shown in Figs. 1(c) and 1(d), with the applied volume of the antisolvent increasing from 500 to 700 μL , the number of pinholes rather decreases. In addition, the thicknesses of the perovskite layer obtained through the cross-sectional FESEM images were 371 ± 13 , 363 ± 10 , 362 ± 12 , and 346 ± 27 nm for applied volumes ranging from 100 to 700 μL , respectively. As shown in Fig. 1(h), the perovskite grain structure collapses and sinks due to the excessive generation of pinholes. Such a small thickness impairs the light harvesting capacity of the perovskite absorption layer [14]. As the antisolvent application volume increases, the application time increases, which means that the reaction time between the perovskite precursor solution and the antisolvent increases. Therefore, although EA is used as an antisolvent for the perovskite precursor material, the reaction with perovskite can be questioned. Taylor *et al.* noted that some of the commonly used antisolvents can dissolve organic halides in mixed cation perovskite precursor materials [15]. From this viewpoint, as the reaction time between the perovskite precursor solution and the antisolvent increases, the antisolvent penetrating the perovskite film continuously dissolves some amount of methylammonium iodide and volatilizes therein through annealing to generate multiple pinholes.

PL and TRPL measurements were performed to investigate the optical properties of the perovskite film in terms of the volume change in the applied antisolvent. Figure 2 shows the PL spectra of the $\text{MAPbI}_3/\text{SnO}_2/\text{ITO}$ films with different volumes of the antisolvent applied at room temperature (293 K). The PL peaks of all the samples appear at approximately 774 nm; however, there is little difference in the PL intensity. The PL intensity is known to increase with a decrease in the

Figure 2. Room-temperature PL spectra of perovskite films prepared with antisolvent of different volumes.

Figure 3. (a) PL decay curves and (b) average PL lifetime of perovskite films prepared with antisolvent of different volumes.

number of defects on the surface, because of the reduced area of the perovskite grain boundaries [16]. On the other hand, it has been reported that the diffusion length of carriers decreases as the grain size decreases, consequently increasing the radiative recombination due to an increase in spatial confinement [17]. Therefore, it is difficult to distinguish the change in the PL intensity in our perovskite film because it includes both the decrease in the grain size and the complexity of pin-hole generation. Moreover, the effect of transport of the carriers generated in the perovskite to the electrode through the electron transport layer due to the deposition on the SnO_2 layers cannot be neglected.

To clearly distinguish these complex changes in carrier dynamics, TRPL measurements were performed. For all the samples, the PL decay curves were measured at the same PL peak position. The PL lifetime and amplitude of each fast and slow component were obtained through a binomial exponential function fitted for the measured PL decay curves, and the average PL lifetime was calculated using the equation $\tau_{\text{avg}} = (A_{\text{fast}}\tau_{\text{fast}}^2 + A_{\text{slow}}\tau_{\text{slow}}^2) / (A_{\text{fast}}\tau_{\text{fast}} + A_{\text{slow}}\tau_{\text{slow}})$ [18]. As illustrated in Figs. 3(a) and 3(b), the PL decay becomes slower with the increase in the applied volume of the antisolvent, and the corresponding average PL lifetimes are 55.7 (100 μL), 58.2 (300 μL), 60.2 (500 μL), and 85.3 ns (700 μL). This phenomenon is related to the increase in the number of pinholes generated in the perovskite film with increasing volume of the applied antisolvent. In the case of the sample with the smallest amount (100 μL) of antisolvent applied, a uniform perovskite film without pinholes could be obtained. To exclude the extraction effect of the photogenerated electrons by the SnO_2 electron transport layer, the PL and TRPL results of the MAPbI_3 film deposited directly on the glass substrate are shown in Figs. 4(a) and 4(b). All the samples show similar PL intensities, except for the 100 μL sample, which shows about half the intensity compared to the others. The weak PL intensity of the 100 μL sample can be attributed to the in-

Figure 4. (a) PL spectra and (b) PL decay curves of perovskite films on a glass substrate.

complete phase transition from the perovskite intermediate phase to the perovskite phase given the low volume of antisolvent used. The average PL lifetime obtained from the PL decay curves in Fig. 4(b) is the fastest for the 100 μ L (59.8 ns) sample, the slowest for the 300 μ L (93.7 ns) sample, and gradually becomes faster as the antisolvent application volume increases from 500 (84.4 ns) to 700 μ L (71.5 ns). The fast decay of the 100 μ L sample can be explained by the deterioration of the perovskite film due to the incomplete extraction of the host solvent, DMF. On the other hand, the decrease in the PL lifetime with increasing antisolvent volume can be explained by the generation of defects due to the increase in the number of pinholes. Although it has indistinguishable PL intensity from the other samples, it shows the possibility of manufacturing a high-efficiency perovskite solar cell device by enabling a fast lifetime owing to the favorable electron transport unaffected by pinholes. Therefore, when using EA as an antisolvent, it is possible to deposit a high-quality perovskite film by applying an appropriate volume of the antisolvent. However, it should be noted that the original function of the antisolvent may not be achieved if the applied volume is too low.

4. Conclusions

The structural and optical properties of a perovskite film were investigated in terms of the applied volume of EA as the antisolvent used in the perovskite deposition process. The generation of pinholes on the surface and inside the perovskite film increased with increasing volume of the applied antisolvent, and the generation of excessive pinholes collapsed the perovskite grain structure. As the number of pinholes increased, the PL lifetime of the perovskite film rapidly increased from 55.7 to 85.3 ns, confirming that pinholes prevented the transport of photogenerated electrons in the perovskite film. This phenomenon could be attributed to the fact that the antisolvent dissolves some of the perovskite precursor material, and applying an appropriate volume of the antisolvent will help in the fabrication of high-quality perovskite-based solar cell devices.

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Conflicts of Interest

The authors have no conflict of interest to declare.

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