

ROLE OF POLAR SOLVENT IN THE SYNTHESIS OF PEROVSKITE  $\text{CH}(\text{NH}_2)_2\text{PbI}_x\text{Br}_{3-x}$  THIN FILMS BY TWO-STEP METHOD FOR THIN-FILM SOLAR CELLS

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Formamidinium  $[(\text{NH}_2)_2\text{CH}^+; \text{FA}]$  lead triiodide ( $\text{FAPbI}_3$ ) perovskite has recently been extensively studied due to better stability with an extension of the optical absorption edge to the infrared region for efficient thin-film solar cells. Recently, interest has extended to the  $\text{FAPbI}_x\text{Br}_{3-x}$  and  $\text{CsFAPbI}_x\text{Br}_{3-x}$  perovskites, which has much higher stability against humidity and a bandgap that is tunable by substitutional doping of Br ions to I sites. Various methods for the fabrication of perovskite thin films have been studied using a one-step solution process and two-step reaction. In a two-step reaction method, porous  $\text{PbX}_2$  ( $X=\text{I}, \text{Cl}, \text{Br}$ ) films and organic halide solutions such as FAX diluted in 2-isopropanol alcohol [IPA;  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ ] solvent are used frequently with *N,N*-dimethylformamide (DMF;  $\text{CH}_3\text{NCHO}$ ) to promote the crystallization of  $\text{PbI}_2$ . The role of the IPA in the synthesis of  $\text{FAPbI}_x\text{Br}_{3-x}$  perovskites is, however, still controversial because the reaction rate is very fast. Here, we present the role of IPA solvent in the synthesis of  $\text{FAPbI}_x\text{Br}_{3-x}$  perovskites using two-step method in terms of spectroscopic ellipsometry (SE), XRD, and FTIR characterizations.

Amorphous (a-) $\text{PbI}_x\text{Br}_{2-x}$  fabricated with DMF/CHP cosolvent was used as a precursor, which were immersed in a solution of  $\text{FAI}_x\text{Br}_{1-x}$  in IPA solvent for various times ( $t_{\text{im}}$ ) at 25°C.  $\text{PbI}_x\text{Br}_{2-x}$  thin films (~150 nm thickness) were prepared on glass by spin coat from a  $\text{PbI}_x\text{Br}_{2-x}$  powder diluted in a DMF/cumene hydroperoxide (CHP;  $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{OOH}$ ) (95:5 v/v) cosolvent to suppress crystallization of  $\text{PbI}_2$ . The refractive index  $n$  and extinction coefficient  $k$  of the corresponding  $\text{FAPbI}_x\text{Br}_{3-x}$  films were determined using SE. The ellipsometric angles,  $\Psi$  and  $\Delta$ , were also measured in the range of 1.5–5.0 eV. The bulk component of optical constants for the perovskite films,  $n$  and  $k$ , and the volume fractions of perovskite and voids ( $f_{\text{perov}}$ ,  $f_{\text{void}}$ ) were determined using a modified amorphous model based on the Forouhi-Bloomer (FB) model combined with three-layer model. Spectral fitting was performed using the optical constant for bulk  $\text{FAPbI}_x\text{Br}_{3-x}$  perovskite, and  $f_{\text{per}}$ ,  $f_{\text{void}}$ , and the film thickness  $d$ , as variables.

Figure 1 shows XRD patterns of  $\text{FAPbI}_x\text{Br}_{3-x}$  films on glass synthesized at various  $t_{\text{im}}$ . The diffraction peaks attributed to the  $\text{FAPbI}_x\text{Br}_{3-x}$  perovskites increased with suppression of the  $\delta$  phase peaks  $\psi$  p と.

Figure 2a shows the best-fit  $n$  and  $k$  spectra for the  $\text{FAPbI}_x\text{Br}_{3-x}$  perovskite bulk at various  $t_{\text{im}}$ . The absorption edge shifted to lower energy from 3.1 to 1.63 eV for 60 s immersion and then became almost independent of  $t_{\text{im}}$ . In addition, fine structures at 2.55, and 3.8 eV were shifted to the infrared region with an increase in their amplitude when  $t_{\text{im}}$  was increased up to 600 s. The layer immersed for 600 s exhibited four fine structures in the  $k$  spectra at 1.63, 2.52, 3.25, and 4.79 eV, which were attributed to the optical transition of the perovskite. The best-fit optical models for the various  $t_{\text{im}}$  are summarized in Fig. 2b.  $f_{\text{void}}$  was increased significantly for the entire film thickness even for only 10 s immersion, which suggests that the rate of crystallization of a- $\text{PbI}_x\text{Br}_{2-x}$  was much quicker than the rate of formation of the perovskite structure. The diffusion of  $\text{FAI}_x\text{Br}_{1-x}$  into the voids and/or grain boundaries resulted in the simultaneous formation of large amounts of free volume and an increase in the film thickness (Fig. 2b), resulting in a decrease in the  $n$ . The  $d$  increased from 150 nm for a- $\text{PbI}_x\text{Br}_{2-x}$  to 350 nm for the  $\text{FAPbI}_x\text{Br}_{3-x}$  perovskites. FTIR also revealed that IPA played a significant role to promote crystallization of the a- $\text{PbI}_x\text{Br}_{2-x}$  film through the removal of residual CPH from the a- $\text{PbI}_x\text{Br}_{2-x}$  network. The diffusion of  $\text{FAI}_x\text{Br}_{1-x}$  into the voids and grain boundaries resulted in the simultaneous formation of large amounts of free volume, resulting in the perovskite structure (Fig. 3).

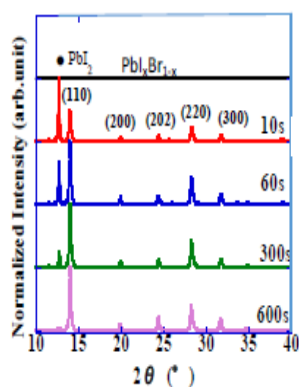


Fig. 1 XRD pattern of  $\text{FAPbI}_x\text{Br}_{3-x}$  films on glass at various  $t_{\text{im}}$ .

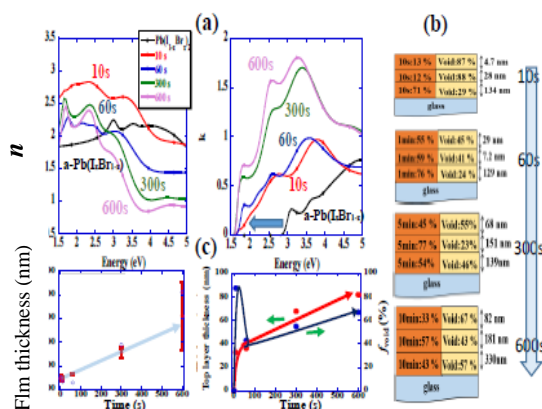


Fig. 2 (a) Best-fit  $n$  and  $k$  spectra for  $\text{FAPbI}_x\text{Br}_{3-x}$  bulk at various  $t_{\text{im}}$ . (b) Best-fit optical models. (c) Total film thickness  $d$ ,  $d_1$  and  $f_{\text{void}}$  in the top layer

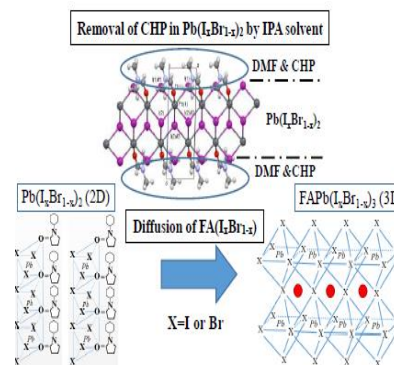


Fig. 3 Mechanism for the formation of  $\text{FAPbI}_x\text{Br}_{3-x}$  perovskites from a- $\text{PbI}_x\text{Br}_{2-x}$  layer and a solution of  $\text{FAI}_x\text{Br}_{1-x}$  in IPA solvent.