# Analysis of Precipitation Process and Modification of Structures and Electrical Properties on $CH_3NH_3PbI_3$ Thin Films for Perovskite Solar Cell Devices

**Yoshiko TSUJI [1, 2 *], Kento Tanaka [2], Yuuki Kominami [2], Enju Sakai [1], and Shintaro Hatamiya [2]**

[1]*Environmental Science Center, The University of Tokyo*
*Hongo 7-3-1, Bunkyo-ku, Tokyo, 113-0033, Japan*

[2]*Department of Chemical System Engineering, The University of Tokyo*
*Hongo 7-3-1, Bunkyo-ku, Tokyo, 113-8656, Japan*

**ISCST-20180918AM-B-PC1**

Presented at the 19th International Coating Science and Technology Symposium, September 16-19, 2018, Long Beach, CA, USA†.

## 1. Introduction

Solution processed solar cell devices using inorganic–organic hybrid compounds with perovskite crystal structure have been intensively studied, since they have high efficiency over 20 % with easy fabrication process. They have attracted increasing attention to improve efficiencies by materials design of inorganic–organic hybrid compounds and novel cell structures. To improve efficiencies, it is also necessary to control the nanostructure of thin films on a macroscale based on a non-equilibrium phenomenon during coating process.

Perovskite compounds, methylammonium lead iodide, are synthesized from $PbI_2$ and $CH_3NH_3I$ ($MAPbI_3$) as following chemical equation;

$$PbI_2 + CH_3NH_3I \rightarrow CH_3NH_3PbI_3$$

Active layer of solar cells requires sufficient film coverage and moderate layer thickness which leads to efficient light absorption. In the coating process, dissolved mixed

* Email of corresponding author: tsuji@esc.u-tokyo.ac.jp

precursor solution of $PbI_2$ and MAI materials react to form methylammonium lead iodide, are precipitated during drying and finally form a film.

In this study, we fabricated perovskite thin films, $MAPbI_3$, by spin coating, investigated the influence of spin-coating rate and the choice of solvents on nanostructure of thin films from the point of precipitation dynamics. We also fabricated $MAPbI_3$ thin films by solid phase diffusion method by ultrasonic spray of MAI solution on spin coated $PbI_2$ to obtain smooth surface morphology.

## 2. Experimental details

### 2-1 Spin coating method

In this study, we used N,N-dimethylformamide (DMF) and gamma-butyrolactone (GBL) as mixed solvents having a DMF/GBL volume ratio of 100/0 to 0/100 and prepared precursor solution of $PbI_2$ and MAI materials of 0.4 mol/L. Films are spin-coated at the desired spin rate, 1000, 2000, or 4000 rpm.

We set up the dynamic observation systems [1]. For film thickness, we monitored the intensity of reflected laser light with 530 nm during spin coating. With the decrease of liquid thickness, constructive interference and destructive interference occur alternately. We also monitored the intensity of scattered laser light with 670 nm during spin coating. At the onset of the formation of the solid phase, the sudden intensity variation film occurs, which should be a critical supersaturation point.

### 2-2 Solid phase diffusion method by ultrasonic spray

The spray deposition is proven as one of the major techniques to deposit a wide variety of materials [2]. The precursor solution was atomized by ultrasonic wave (2.4 MHz), and sprayed on the heated substrate. We tried to form $MAPbI_3$ by ultrasonic atomization method by preparing a mixed solution of $PbI_2$ and MAI using DMF, DMSO and GBL as a solvent. Since $MAPbI_3$ was soluble in the solvent, the film deposition and the etching occur simultaneously and it was difficult to form the uniform film.

On the other hand, in the two-step film formation (Fig. 1), $MAPbI_3$ formed by solid phase reaction of MAI /$PbI_2$, the solvents of the $PbI_2$ solution and the MAI solution can be independently selected, and it is possible to supply MAI using a solvent that does not etch $PbI_2$ and $MAPbI_3$ phase. 80 nm-thick $PbI_2$ film was spin coated using $PbI_2$-DMF solution followed by supplying MAI mist using MAI-ethanol solution by ultra sonic. Substrate temperature during supplying MAI was 100, 125, 150, 175, 200 ° C. The flux ratio of MAI was controlled by the concentration of the solution from 0.1 to 0.2 mol/L and total amount of MAI was controlled by the spraying time from 1 to 8 min.

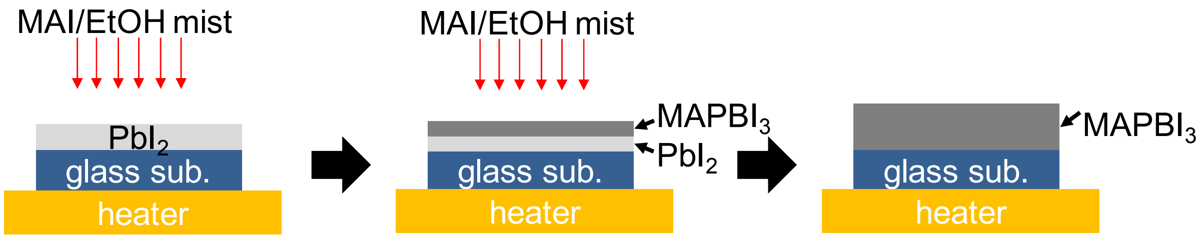


FIG. 1 Solid phase diffusion method by ultrasonic spray

**2-3 Characterization of film properties**

The crystal structures of obtained films were determined by optical microscopy and X-ray diffraction (XRD) analyses. Ultraviolet-visible (UV-Vis) absorption spectra were measured with an absorption spectrophotometer.

**3. Results and discussions**

**3-1 Dynamic observation during spin coating**

At the onset of the formation of the solid phase, the sudden scattering intensity variation occurs in the dynamic observation, which should be a critical supersaturation point. Fig 2 shows the relationship between the degree of supersaturation and spin coating rate. It is found that the degree of supersaturation is increased by increasing the spin coating rate. According to the nucleation theory, precipitation from a solution with high degree of supersaturation increases the nucleation frequency, leading

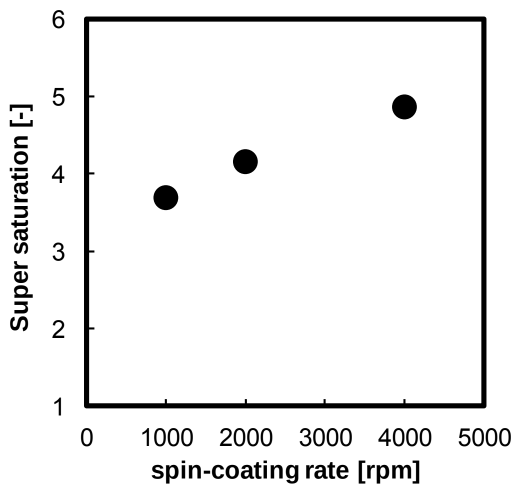


Fig.2 The degree of supersaturation in spin coating process with DMF solvent

an increase in film coverage on the substrate. It was confirmed that the coverage was improved as the increase of spin coating rate from the optical microscopic image of obtained films (FIG. 3).

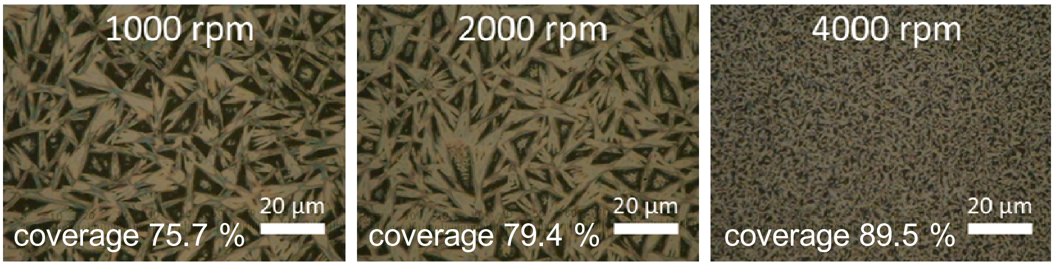


FIG. 3 Optical microscope images of spin coated $MAPbI_3$ films

### 3-2. Effect of mixed solvent in spin coating

When GBL was used as a solvent, the film with a higher coverage and thinner thickness was obtained rather than using DMF as a solvent. To achieve a higher coverage film with enough thickness, the liquid thickness during coating should be controlled by using mixed solvent in addition to realize the nucleation in GBL ambient.

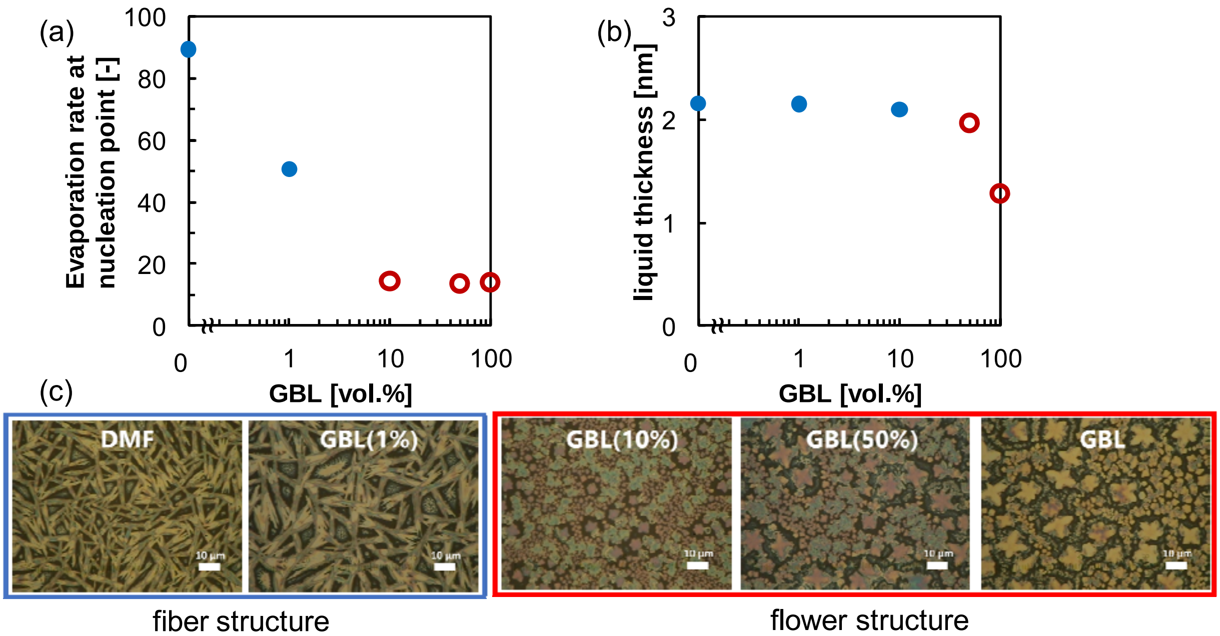


Fig. 4 The effect of mixed solvent on dynamics during coating and film structures

Mixed solvent of DMF and GBL was used, and dynamics during spin coating was observed and found that evaporating rate at nucleation point decreased with the increase of GBL concentration and it became almost constant at more than 10%-GBL (Fig. 4(a). On the other hand, liquid thickness was almost constant below 10%-GBL (Fig. 4(b)). When 10 %-GBL mixed solution was used, we could achieve balance between the nucleation in GBL ambient and thick liquid thickness, causing high density films with high absorbance of visible light.

### 3-3. Two step deposition of $MAPbI_3$

Spin coated $PbI_2$ has uniform structure with high density. It was found that $MAPbI_3$ was formed with the increase of substrate temperature during supplying MAI by spraying, while MAI was desorbed and $MAPbI_3$ was not formed at 175 °C or higher. Fig. 5 shows the XRD of films after solid phase reaction of MAI on $PbI_2$ at 150 °C. When MAI spraying time increased, solid phase reaction between MAI and $PbI_2$ occurred, causing the decrease of intensity of $PbI_2$ and the increase of intensity of $MAPbI_3$. But the intensity of $MAPbI_3$ was constant after 5 min, where supply amount of MAI was saturated for 80 nm-thick $PbI_2$. Uniform coverage of $MAPbI_3$ was achieved by solid phase reaction between MAI and $PbI_2$.

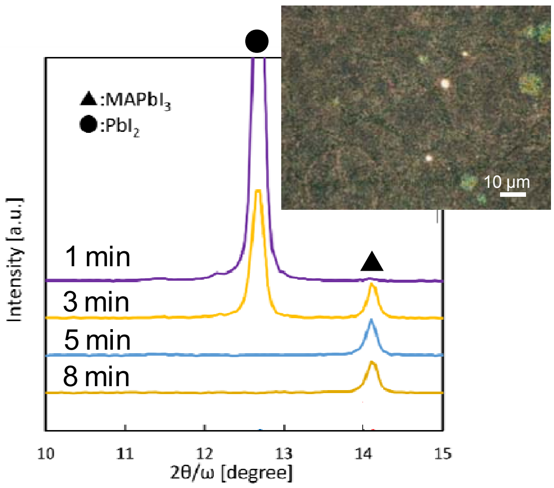

Fig. 5 XRD spectra of two step deposition films

### 4. Conclusion

In order to obtain a perovskite layer having a high absorbance, it is necessary to increase both the coverage and the film thickness. We tried two ways to achieve this problem; the first one was using mixed solvent, which enables compatibility of appropriate solution ambient at precipitation point and improvement of film thickness.

The second one is spin coating of $PbI_2$ followed by supplying MAI mist using MAI-ethanol solution by ultra sonic, which caused solid phase reaction of MAI /$PbI_2$.

References

[1] Y.Tsuji, et al., ISCST2016. [2] S. Golshahi, et al., Thin Solid Films 518, 1149 (2009).