

Thin film fabrication of organic-inorganic halide perovskite by bar-coating method and its blend effect of ammonium chloride

Masashi Murata¹, Meigen Gi¹, Ryotaro Tsuji², Akihiko Fujii¹ and Masanori Ozaki¹

¹ Graduate School of Engineering, Osaka Univ.
2-1 Yamada-oka, Suita, Osaka 565-0871, Japan

² Material Solutions Research Institute, KANEKA Corp. Osaka, Japan
E-mail: afujii@opal.eei.eng.osaka-u.ac.jp

Abstract

Thin films of organic-inorganic halide perovskite, $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃), were fabricated by a bar-coating method, which is a candidate technique for large-scale production. Using the bar-coating method, the large grains and uniaxial orientation of crystal axis of MAPbI₃ were realized. In addition, the grain boundaries in the thin film were suppressed by blending NH_4Cl .

1. Introduction

Organic-inorganic halide perovskite photovoltaics have been intensively studied, because of their high performance, cost effectiveness and easy fabrication process. A typical material used in the active layer are described by ABX_3 perovskite structure (A = organic cation, B = metal cation, X = halide anion) as showed in Fig. 1, and possesses the outstanding optoelectronic and carrier transport properties [1][2]. Recently, the power conversion efficiency of the photovoltaic cells using this kind of material achieved to be 24.2% [3], which is comparable to crystalline Si solar cells. Spin-coating method is used to obtain a uniform perovskite active layer in general. Since rotating a substrate at high speed must be necessary in the spin-coating method, there are difficulties in adapting to large-size substrates. Hence, the appropriate method for the industrial mass-production should be developed.

In this study, we adopted a bar-coating method to fabricate thin films of $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃), because of the effectiveness for large-scale production. In addition, NH_4Cl was blended to precursor solution in order to improve the film quality. The film formation mechanism was discussed by taking the crystallinity of MAPbI₃ films and grain structure into consideration.

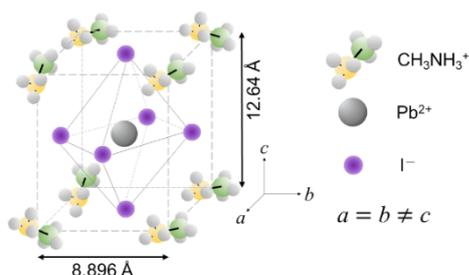


Fig. 1 Unit cell of MAPbI₃ in tetragonal phase at room temperature.

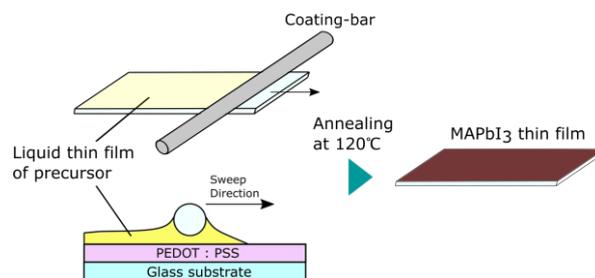


Fig. 2 Schematic diagram of fabrication processes of perovskite thin film by the bar-coating method.

2. Experimental

Thin films of MAPbI₃ were fabricated in the following process (Fig. 2). Solution of perovskite precursor was prepared by dissolving PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ in dimethyl sulfoxide at each concentration of 1 M. Glass substrates were cleaned with a cleaning agent and distilled water by ultrasonication, then UV-ozone treatment. PEDOT:PSS layer was fabricated onto the substrate by spin-coating at 3000 rpm for 60 s, then annealing at 140 °C for 10 min. The prepared precursor solution was dropped onto a coating-bar, which was set above the substrate, then moved the coating-bar in the horizontal direction at a constant speed of 200 $\mu\text{m/s}$, resulting in the liquid thin films on the substrate. Finally, MAPbI₃ thin film was obtained by annealing the substrate at 120 °C.

Absorption spectrum of the thin film was measured by UV-Vis spectrometer (Shimadzu, UV-3150). The crystal structure was confirmed by XRD (Rigaku, SmartLab), and the surface morphology was observed by a laser microscope (KEYENCE, VK9710) and FE-SEM (HITACHI, S-4300).

3. Results and discussion

The thin films fabricated by the bar-coating method was dark brown color and seemed to be uniform on the substrate. In the absorption spectrum of the thin film, typical spectrum with characteristic peaks of MAPbI₃ at 460 nm and 780 nm [4] was obtained. Therefore, it is noted that the MAPbI₃ thin films were actually fabricated by the bar-coating method and annealing process.

The out-of-plane XRD patterns of the thin films fabricated by spin-coating and by bar-coating are showed in Fig. 3. The spin-coating film exhibited the similar peaks with those observed in the powder samples [5], in contrast, the bar-coating film exhibited particularly strong peaks at 20 ° and 40.7 °.

MAPbI₃ is based on a tetragonal phase in room temperature [6], and these peaks are corresponding to the diffractions of (200) and (400) planes, respectively. It is considered, therefore, that the *a*-axis shown in Fig. 1 was oriented in the perpendicular direction to the substrate.

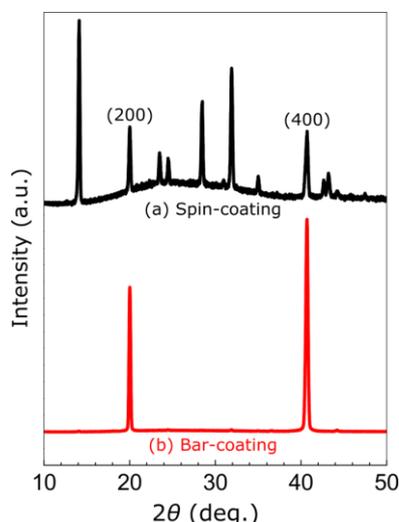


Fig. 3 XRD patterns of the MAPbI₃ thin films fabricated by spin-coating (anti-solvent process) (a) and bar-coating (b).

Observed the thin film surface shape by the laser microscope, large-size grains of approximately 100 μm as shown in Fig. 4 (a), which were much larger than those in the spin-coated films with a typical anti-solvent process, appeared. In the bar-coating process, as the poor solvent drop like the anti-solvent process was not carried out, the active nucleation could be suppressed. Therefore, the microcrystals grew from a small number of nuclei in the annealing process, resulting in the large-size grains throughout the thin film. Such expansion of the grain size should be effective for carrier transport owing to the suppression of structural defects [7]. However, the grain boundary must be a crucial problem for the solar cell performance due to the reduction of shunt resistance in equivalent circuit.

In order to eliminate the grain boundary and improve film morphology, NH₄Cl was blended to the precursor solution. It was previously reported that NH₄Cl retarded the crystallization of MAPbI₃ and interconnected the separated crystals of MAPbI₃ through forming the intermediate [8]. Figure 4 (b) shows the microscope image of the thin film surface when 0.25 M of NH₄Cl was blended.

Comparing with the case without NH₄Cl in Fig. 4 (a), the gaps between the grains disappeared, and the film surface seems to be uniform in a large area by using NH₄Cl, that might be explained by the control of nucleation. The films of MAPbI₃ should be formed by collision and coalescence of island-shaped crystals grown from nuclei according to the Volmer-Weber growth mode [9]. In the bar-coating method without blending NH₄Cl, the delayed nucleation occurred before the crystal growth and collision, that is one of the reasons for the grain boundary generation. On the other hand, the

blend of NH₄Cl was effective for suppressing the nucleation as well as crystal growth through the formation of intermediates.

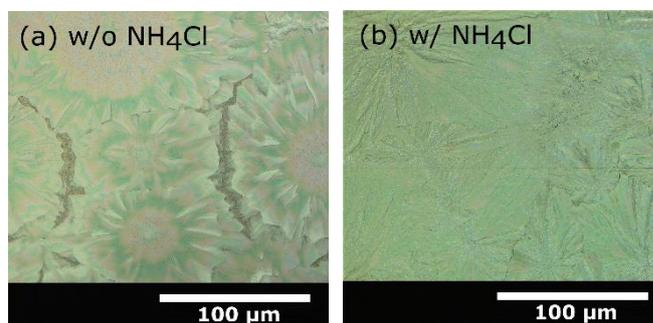


Fig. 4 Microscope images of MAPbI₃ thin films fabricated by bar-coating without NH₄Cl (a) and with NH₄Cl (b).

4. Conclusions

The MAPbI₃ thin film was fabricated by the bar-coating method, and demonstrated the uniaxial orientation of the *a*-axis. Blending NH₄Cl was effective to improve the thin film morphology owing to control the nucleation as well as crystal growth. The bar-coating method must be a suitable method for fabricating large-scale organic-inorganic halide perovskite thin films.

Acknowledgements

We thank prof. Yuko Takeoka of Sophia University and prof. Shusaku Nagano of Nagoya University, and Dr. Quang-Duy Dao of Vietnam National University, Hanoi for fruitful discussion on the thin film fabrication and XRD analysis. This work was partly supported by the JSPS KAKENHI Grant Numbers 17K18882 and 18H04514, and the JSPS Core-to-Core Program A., Advanced Research Networks, the Nanotechnology Platform Program (Molecule and Material Synthesis) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

References

- [1] W.-J. Yin, T. Shi, and Y. Yan, *Adv. Mater.* **26** (2014) 4653.
- [2] S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. P. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza and H. J. Snaith, *Science* **342** (2013) 341.
- [3] <https://www.nrel.gov/pv/cell-efficiency.html> (accessed 2019)
- [4] G. Xing, N. Mathews, S. Sun, S. S. Lim, Y. M. Lam, M. Grätzel, S. Mhaisalkar and T. C. Sum, *Science* **342** (2013) 344.
- [5] G. P. Nagabhushana, R. Shivaramaiah, and A. Navrotsky, *Proc. Natl. Acad. Sci.* **113** (2016) 7717.
- [6] A. M. A. Leguy, A. R. González, J. M. Frost, J. Skelton, F. Brivio, X. R. Martínez, O. J. Weber, A. Pallipurath, M. I. Alonso, M. C. Quiles, M. T. Weller, J. Nelson, A. Walsh and P. R. F. Barnes, *Phys. Chem. Chem. Phys.* **18** (2016) 27051.
- [7] W. Nie, H. Tsai, R. Asadpour, J.-C. Blancon, A. J. Neukirch, G. Gupta, J. J. Crochet, M. Chhowalla, S. Tretiak, M. A. Alam, H.-L. Wang and A. D. Mohite, *Science* **347** (2015) 522.
- [8] Y. Rong, X. Hou, Y. Hu, A. Mei, L. Liu, P. Wang and H. Han, *Nat. Commun.* **8** (2017) 14555.
- [9] Y. C. Zheng, S. Yang, X. Chen, Y. Chen, Y. Hou, and H. G. Yang, *Chem. Mater* **27** (2015) 5116.