Conference materials UDC 53.093 DOI: https://doi.org/10.18721/JPM.163.110

Optimization of triple-cation perovskite thin films by PEAI additive

D.A. Tatarinov¹ , A.P. Pushkarev¹, S.V. Makarov^{1, 2}.

¹ ITMO University, St. Petersburg, Russia;

² Qingdao Innovation and Development Center, Harbin Engineering University, Qingdao, China.

^{III} dmitry.tatarinov@metalab.ifmo.ru

Abstract. This work presents an additive engineering approach to prepare structurally stable highly crystalline triple-cation and mixed-anion perovskite thin film by using 5 mol% doping of perovskite solution with phenethylammonium iodide (PEAI). Such an additive provides increase in grain size up to 20 % and preserves surface morphology of non-encapsulated films for at least 6 months at ambient conditions. Stability experiments showed excellent results for films with PEAI additive, which confirmed by X-ray diffraction measurements. The additive strategies have great potential to improve the power conversion efficiency and the long-term stability of the perovskite solar cell suitable for commercialization.

Keywords: halide perovskites, additive engineering, surface morphology

Funding: The work was supported by the Ministry of Science and Higher Education of the Russian Federation (Project 075-15-2021-1349).

Citation: Tatarinov D.A., Pushkarev A.P., Makarov S.V., Optimization triple-cation perovskite thin films by PEAI additive, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.1) (2023) 59–63. DOI: https://doi.org/10.18721/JPM.163.110

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 53.093 DOI: https://doi.org/10.18721/JPM.163.110

Оптимизация тонких пленок перовскита с тройным катионом с помощью добавки PEAI

Д.А. Татаринов¹ ⊠, А.П. Пушкарев¹, С.В. Макаров^{1, 2}

¹ Университет ИТМО, Санкт-Петербург, Россия;

² Центр инноваций и развития Циндао, Харбинский инженерный университет, Циндао, Китай. dmitry.tatarinov@metalab.ifmo.ru

Аннотация. В этой работе представлен новый подход аддитивной инженерии для получения структурно высокостабильной кристаллической тонкой пленки перовскита с тройным катионом и смешанными анионами с использованием 5% молярного легирования раствора перовскита йодидом фенэтиламмония (PEAI). Такая добавка обеспечивает увеличение размера зерна до 20% по сравнению с пленкой без использования PEAI и сохраняет морфологию поверхности некапсулированных пленок не менее 6 месяцев в условиях окружающей среды. Эксперименты по стабильности показали отличные результаты для пленок с добавкой PEAI, что было подтверждено измерениями дифракцией рентгеновского излучения. Аддитивные стратегии обладают большим потенциалом для улучшения коэффициента преобразования энергии и долгосрочной стабильности перовскитных солнечных элементов, пригодных для коммерческого использования.

Ключевые слова: галогенидные перовскиты, аддитивная инженерия, морфология поверхности

© Tatarinov D.A., Pushkarev A.P., Makarov S.V., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Финансирование: Работа выполнена при поддержке Министерства науки и высшего образования Российской Федерации (проект 075-15-2021-1349).

Ссылка при цитировании: Татаринов Д.А., Пушкарев А.П., Макаров С.В. Оптимизация тонких пленок перовскита с тройным катионом с помощью добавки РЕАІ // Научнотехнические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.1. С. 59–63. DOI: https://doi.org/10.18721/JPM.163.110

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Metal-organic perovskites have shown rapid progress in the field of high-performance optoelectronics. The most notable progress has been made in the field of perovskite photovoltaics [1–3]. For example, today the efficiency of energy conversion in single-junction perovskite solar cells is 25.7 % [4], which in turn makes these devices competitive with existing technologies based on polycrystalline silicon and CIGS. The remarkable performance of lead halide perovskites in solar cells can be attributed to their long carrier lifetimes and high carrier mobility. However, there are still problems such as J-V curves hysteresis, ion migration, low resistance to oxygen and moisture that prevent perovskites from large-scale production of the devices showing long-term operation. The efforts of the scientific community have been aimed at solving these problems, for example, by introducing additional passivating layers and searching for new perovskite compositions [5]. From this point of view, multi-cation perovskite films passivated with large-molecule ammonium salts seems a promising solution.

Materials and Methods

Materials: Cesium iodide (CsI, Sigma Aldrich), methylammonium bromide (MaBr, DyeSole), formammidinium iodide (FAI, DyeSole), lead (II) bromide (PbBr₂, 99.99 % pure, TCI Chemicals), lead (II) iodide (PbI₂, 99.99% pure, TCI chemicals), dimethyl sulfoxide (DMSO, anhydrous \geq 99.8 %, Sigma Aldrich), N,N-dimethylformamide (DMF, anhydrous \geq 99.8 %, Sigma Aldrich) and chlorobenzene (anhydrous, Sigma-Aldrich) were used as supplied and without additional purification.

In this work, we used two types of solution to formation perovskite thin films – reference solution CsFAMAPbBrI and with 5 mol% Phenethylammonium iodide (PEAI) additive. We prepare reference solution by dissolving 15.6 mg CsI, 15.7 mg MABr, 171.97 mg FAI, 73.4 mg PbBr₂ and 507.4 mg PbI₂ in the mixture of DMF:DMSO in a relation equal to 4:1. Second solution with 5 mol% additive observed with the same concentrations and additive of 12.45 mg PEAI. These solutions filtered by PTFE filter before depositions on glass substrates. Glass substrates prepared by wash in with sonication the NaOH solution, deionized water, acetone and 2-propanol for 10 minutes consecutively, and then exposed to UV ozone for 15 minutes to obtain a hydrophilic surface. Afterwards substrates transferred in the dry glovebox with nitrogen atmosphere. The deposition of perovskite thin films on prepared substrates by single-step spin-coating method at 3000 rpm for 5 minutes. At the 30 second after the start 350 µl of the antisolvent (chlorobenzene) dripped on the top of the rotating substrate. After that samples moved for the hot play and annealed at 90 °C for 10 min to remove solvent residues.

The morphology and thicknesses of resulting films were evaluated by a scanning electron microscope (FEI Quanta Inspect) and a surface profiler (KLA Tencor: P-7). We studied how additive affects the surfaces roughness of observed films by using atomic force microscopy method.

The quality of crystallinity of the observed films and study of degradation in ambient conditions for reference films and 5% additive made by XRD experiments at X-ray diffractometer SmartLab (Rigaku IV) equipped with a 9 kW rotating Cu anode X-ray tube.

Results and Discussion

Atomic-force microscopy, scanning electron microscopy, stylus profilometry was used to prove effect additive of PEAI on morphologies of observed films. Each films with and w/o additive

[©] Татаринов Д.А., Пушкарев А.П., Макаров С.В. 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

shows same thickness 500 ± 10 nm, which were verified by the stylus profilometer KLA Tencor: P-7 (Fig. 1, *a*). Inspection of the surface morphology by atomic force microscopy (AFM) shows reduction of the roughness for the perovskite film with additive of PEAI by 2 times relative to the reference film (Fig. 1, *b*-*c*).



Fig. 1. Structure characterisation of mixed-cation perovskite films w/o and with 5 % additive of PEAI - (a) thickness of CsFAMAPbIBr (reference) film and perovskite film with 5 % PEAI additive by stylus profilometry; AFM microphotographs of surfaces roughness for thin perovskite films – reference (b) and with 5 mol% additive of PEAI (c); SEM images of perovskite films – reference (d) and with 5 mol% PEAI (e)

Scanning electron microscopy (SEM) images visualized grain sizes for pure CsFAMAPbIBr and CsFAMAPbIBr with 5 mol% additive of PEAI films (Fig. 1, d, e). Notably, grain's size of perovskite film with PEAI additive into solution increase for 20 % compared with the reference film, the average size of grains in reference film was 166 nm and 202 nm for film with PEAI additive, respectively. This probably indicate changes in morphological modification by additive phenethylammonium iodide into triple-cation and mixed anion perovskite solution.

We studied crystallinity and behavior of the degradation process of observed films by X-ray diffractions method. The perovskite film with PEAI additive demonstrated new XRD patterns (060), (111), (002), (003) compared to pure CsFAMAPbIBr film (Fig. 2, *a*, *d*). Peak at (060) indicate Ruddelsden-Popper phase of perovskite structure [6], which appeared about by adding PEAI into perovskite solutions, rest peaks shows that crystallinity of this film higher than for reference film, which have only three peaks on perovskite phase. We can explain the presence of the lead iodide peak in both films by using an excess of PbI₂ in preparing the solution. On the first stage of degradation of the perovskite film with PEAI additive (cracks and pinholes appeared on the surface) we saw peak enhancement of the Ruddelsden-Popper phase (060), (080) compared to decreasing of perovskites peaks (Fig. 2, *b*).

To study the effect of adding 5 % PEAI to the composition of the perovskite solution, we left the obtained films without PEAI and with PEAI in the ambient atmosphere at a temperature of 19-22 °C and a relative humidity of 20-30 %. Notably, the studied films were not encapsulated or protected from external environmental influences. The condition of the films have been monitored for 6 months. Figure 3 shows the visual results of the stability experiments of the films produced during the study period. The pure triple-cation and mixed anion perovskite film completely converted to the non-conducting yellow phase within 3 months (Fig. 3, c), which is also confirmed by the XRD pattern obtained by X-ray diffraction measurements (Fig. 2, e).



Fig. 2. XRD patterns of observed thin perovskite films. Fresh CsFAMAPbIBr film with PEAI additive (a); 1 stage degradation of the film with 5 mol% PEAI (b); fully conversion CsFAMAPbIBr with PEAI to yellow non-conductive phase (c); fresh reference film without PEAI additive (d); degraded CsFAMAPbIBr film w/o PEAI (e)

Unlike the reference film, the perovskite film with 5 mol% PEAI did not show any visible changes on surface quality after 3 months of observation (Fig. 3, d).

Moreover, after 6 months study of the obtained films stability, the perovskite film with additive of PEAI did not completely pass into the non-conductive phase, a discontinuity of the film was observed due to the appearance of a large number of pinholes, however, the color remained the same as the initial film (Fig. 3, f). A complete transition to the yellow (non-conductive phase) for this film was observed after 9 months, which, as in the case of the reference film, is confirmed by XRD measurements (Fig. 2, c).



Fig. 3. Illustration of perovskite films degradation for the period of stay in the ambient condition without any passivation or encapsulation – fresh reference film (a); fresh CsFAMAPbIBr film with 5 mol% additive of PEAI (b); reference film after 3 months (c); with PEAI after 3 months (d); reference after 6 months (e); with PEAI after 6 months (f)

We have demonstrated experimentally that additive of 5 mol% Phenethylammonium iodide (PEAI) into perovskite solution improve size of perovskite crystalline grains and decrease the surface roughness of observed films compared to pure CsFAMAPbIBr thin films. Moreover, this additive engineering play huge role on the stability of observed films, which will be use as a photoactive layer in perovskite solar cells, perovskite light-emitting devices and other optoelectronic applications.

Conclusion

We demonstrate the newest method of improving quality and stability of triple-cation and mixed anion thin films perovskite. Additive into perovskite solution increase grain's sizes of resulting films up to 20 %, showed incredible stability at ambient conditions for 6 months without any encapsulations. This kind of films can be used in optoelectronic devices as a photoactive layer to improve quality and stability for whole devices. The additive strategies have great potential to improve the power conversion efficiency and the long-term stability of the perovskite solar cell suitable for commercialization.

Acknowledgments

The work was supported by the Ministry of Science and Higher Education of the Russian Federation (Project 075-15-2021-1349).

REFERENCES

1. Snaith H.J., Perovskites: The emergence of a new era for low-cost, high-efficiency solar cells. The Journal of Physical Chemistry Letters, 4 (2013) 3623–3630.

2. Stranks S.D., Snaith H.J., Metal-halide perovskites for photovoltaic and light-emitting devices. Nat. Nanotechnol, 10 (2015) 391–402.

3. D'Innocenzo V., Grancini G., Alcocer M.J. P., Kandada A.R.S., Stranks S.D., Lee M.M., Lanzani G., Snaith H.J., Petrozza A., Excitons versus free charges in organo-lead tri-halide perovskites. Nat. Commun, 5 (2014) 3586.

4. National Renewable Energy Laboratory, URL: https://www.nrel.gov/pv/assets/pdfs/best-research-cell-efficiencies-rev211214.pdf.

5. Tang. G., You. P., Tai. Q., Wu. R., Yan. F., Performance Enhancement of Perovskite Solar Cells Induced by Lead Acetate as an Additive. Sol. RRL, 2 (2018) 1800066.

6. Vázquez-Cárdenas R., Rodríguez-Romero J., Echeverría-Arrondo C., Sanchez-Diaz J., Chirvony V.S., Martínez-Pastor J.P., Díaz-Leyva P., Reyes-Gymez J., Zarazua I., Mora-Sery I., Suppressing the Formation of High n-Phase and 3D Perovskites in the Fabrication of Ruddlesden–Popper Perovskite Thin Films by Bulky Organic Cation Engineering. Chemistry of Materials, 34 (2022) no. 7 3076–3088.

THE AUTHORS

TATARINOV Dmitry A. dmitry.tatarinov@metalab.ifmo.ru ORCID: 0000-0002-4825-9041 MAKAROV Sergey V. s.makarov@metalab.ifmo.ru ORCID: 0000-0002-9257-6183

PUSHKAREV Anatoly P. anatoly.pushkarev@metalab.ifmo.ru ORCID: 0000-0002-1793-6812

Received 05.07.2023. Approved after reviewing 07.08.2023. Accepted 07.08.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023