Pin-Hole Free Perovskite Film for Solar Cells Application Prepared by Controlled Two-Step Spin-Coating Method

A Bahtiar¹, S Rahmanita¹ and Y D Inayatie¹

¹Department of Physics, Universitas Padjadjaran
Jl. Raya Bandung-Sumedang km. 21 Jatinangor, Sumedang Indonesia 45363
E-mail: ayi.bahtiar@phys.unpad.ac.id

Abstract. Morphology of perovskite film is a key important for achieving high performance perovskite solar cells. Perovskite films are commonly prepared by two-step spin-coating method. However, pin-holes are frequently formed in perovskite films due to incomplete conversion of lead-iodide (PbI₂) into perovskite CH₃NH₃PbI₃. Pin-holes in perovskite film cause large hysteresis in current-voltage curve of solar cells due to large series resistance between perovskite layer-hole transport material. Moreover, crystal structure and grain size of perovskite crystal are also other important parameters for achieving high performance solar cells, which are significantly affected by preparation of perovskite film. We studied the effect of preparation of perovskite film using controlled spin-coating parameters on crystal structure and morphological properties of perovskite film. We used two-step spin-coating method for preparation of perovskite film with varied spinning speed, spinning time and temperature of spin-coating process to control growth of perovskite crystal aimed to produce high quality perovskite crystal with pin-hole free and large grain size. All experiment was performed in air with high humidity (larger than 80%). The best crystal structure, pin-hole free with large grain crystal size of perovskite film was obtained from film prepared at room temperature with spinning speed 1000 rpm for 20 seconds and annealed at 100°C for 300 seconds.

1. Introduction
Recently, perovskite materials have been intensively studied as active material for high power conversion efficiency (PCE) solar cells due to their wide light absorption spectrum and can be processed into thin films using low-cost techniques, therefore, the perovskite materials are good candidate for large scale production and mass utilization of solar cells replacing high-cost conventional solar cells, such as silicon and germanium arsenide. Today, state-of-the-art PCE of perovskite solar cell is reached more than 21% which is comparable to conventional and market available silicon based solar cell [1]. However, reproducibility issue is a main problem to fabricate this solar cell in large scale. The difficulty to control morphology of perovskite films is a cause of large variation of the PCE of solar cells. The main strategic issues for improving the PCE and its reproducibility are control morphology of perovskite films and to understand charges carrier transport in active material.

Methylammonium lead (III) iodide (CH₃NH₃PbI₃) material is the most popular material used as active material for perovskite solar cells because it has a direct bandgap of ~ 1.55 eV, corresponding to an absorption onset at 800 nm and intense absorption of the entire visible spectrum [2-3]. These properties are expected to produce solar with PCE comparable with high-cost conventional inorganic solar cells such as silicon and germanium arsenide. Moreover, the exciton binding energy of this material is very...
small and has long exciton diffusion length in the order of 100 -1000 nm with lifetime of ~ 100 ns [4-5], so this perovskite material promises great potential for high performance solar cells with low-cost and large scale production.

Perovskite material was firstly used as light absorber for liquid dye-sensitized solar cell by Miyasaka et al with a PCE of only 3.8% [6]. However, a significant improvement of PCE was obtained by replacing the liquid hole transport material (HTM) with the solid 2,2’,7,7’-tetakis(N,N-di-p-methoxyphenylamine)-9,9’;spirobifluorene (Spiro-OMeTAD) to hinder the dissolution of perovskite material [7-10]. Snaith et al [11] has successfully prepared a solid-state Al2O3 mesoscopic solar cells using CH3NH3PbI3 as active material with PCE of 10.9%. They also successfully fabricated the perovskite solar cells without mesoscopic layer through control morphology of perovskite film [12]. Graetz et al used two-step sequential deposition method for producing uniform morphology of perovskite film and a PCE higher than 15% was achieved [13]. Recently, Yang et al reported planar perovskite solar cells with PCE of 19.3% by efficient interface engineering [14]. The world record of more than 21% PCE of perovskite solar cell is already reported [15].

Although, the 20% psychological barrier of PCE solar cells for large scale production is already exceeded, but there are some problem must be solved. First, the problem of hysteresis curve in solar cells characteristic, due to some problem in high quality perovskite film with pin-hole free and large grains size, the interface between perovskite material, hole transport layer and electron transport layer which causes the inaccuracy in evaluating the PCE. Second, the most crucial issue for PCE is to control morphology of perovskite film as active material of solar cells. Many photo-physical properties, such as light absorption, charge carrier transport and diffusion length can be dramatically influenced by the crystallization of the perovskite film. The defects and the crystal grains act as charges carrier traps which would encourage the electron recombination and hence would affect the PCE of solar cells. Third, the problem related to the reproducibility of the measured PCE of solar cells due to the difficulty to control perovskite film morphology. Therefore, the device performance strongly depends on the morphology of the perovskite film [12,15-18].

Here, we reported our recent study on preparation perovskite CH3NH3PbI3 films with high quality crystal and large scale grains (larger than 500 nm) through controlled parameters of two-step spin coating method in air with high humidity. We varied spinning speed, spinning time and temperature of spin-coating process to control growth of perovskite crystal aimed to produce high quality perovskite crystal with pin-hole free and large grain size. We obtained the best crystal structure, pin-hole free with large grain crystal size of perovskite film was obtained from film prepared at room temperature with spinning speed 1000 rpm for 20 seconds and annealed at 100°C for 300 seconds. These parameters can be used as standard method for preparing high quality perovskite crystal with large grains size in air with high humidity (> 80%) to produce high PCE of solar cells.

2. Experimental Method
Lead(II) iodide or PbI2 and methylammonium iodide (CH3NH3I, MAI), poly(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) (PEDOT:PSS) solution were purchased from Luminescence Technology Inc. Taiwan and used as received. Dimethylformamide (DMF) and 2-isopropanol (IPA) solvents were purchased from Sigma Aldrich and used without further purification. The PbI2 solution was prepared by dissolving of 900 mg PbI2 in 2 ml DMF. The solution was heated while stirred at 70°C for 24 hours. After heating and stirring process, the solution was centrifuged with a speed of 4000 rpm for 15 minutes to obtain homogeneous solution. The homogeneous PbI2 solution was confirmed by yellow transparent solution. Meanwhile, the MAI solution was prepared by putting 90 mg MAI in 2 ml IPA and heated at 70°C for 30 minutes while stirred using magnetic stirrer.

Perovskite films were prepared with two-step spin-coating method on PEDOT:PSS film spin-coated on glass substrate. PEDOT:PSS solution was spin-coated on cleaned glass substrate with spinning speed 1000 rpm for 20 seconds. The PEDOT:PSS film was annealed at 110°C for 20 minutes. In two-step spin-coating method, PbI2 film was first spin-coated onto PEDOT:PSS film and subsequently followed by spin-coated of MAI solution. Three perovskite films were prepared with different spin-coating
parameters and different treatment of annealing temperatures after spin-coating films, as shown in Table 1. We used two-step annealing temperature at variation-1 and variation-3. All solutions and films preparation were conducted in air with high humidity (> 80%). Crystal structure perovskite films were measured by XRD and SEM was used to analyze perovskite film morphology.

**Table 1.** Spin-coating and annealing parameters of preparation thin films perovskite

| Variation | Solutions | Temperature of PbI₂ before spin-coating of MAI (°C) | Spin-coating parameters | Annealing temperature (°C) | Annealing time (s) |
|-----------|-----------|---------------------------------------------------|--------------------------|---------------------------|-------------------|
| 1         | PbI₂      | 100                                               | 1000                     | 20                        | 40                |
|           | MAI       | Room Temperature                                  |                          |                           | 180               |
|           |           |                                                   |                          |                           | 100               |
|           |           |                                                   |                          |                           | 300               |
| 2         | PbI₂      | Room Temperature                                  | 6000                     | 35                        | 70                |
|           | MAI       | Room Temperature                                  |                          |                           | 300               |
| 3         | PbI₂      | Room Temperature                                  | 1000                     | 20                        | 40                |
|           | MAI       | Room Temperature                                  |                          |                           | 180               |
|           |           |                                                   |                          |                           | 100               |
|           |           |                                                   |                          |                           | 300               |

3. Results and Discussion

Figure 1 shows XRD patterns of PbI₂ and perovskite films spin-coated on PEDOT:PSS coated glass. PbI₂ film was oriented in c-axis only as indicated by four main peaks at 12.7°, 24.6°, 38.7°, and at 52.4° that shows crystal orientation at (001), (002), (003), and (004), respectively [13]. PbI₂ films prepared at 70°C and room temperature have similar XRD pattern which shows that PbI₂ crystal is not affected by spin-coating temperature from homogeneous and yellow transparent solution of PbI₂. In perovskite variation-1 film shows diffraction peaks at 14.2°, 24.6°, 28.5°, 31.8°, 40.5°, 44.0°, and at 50.3° which correlation to crystal plane of (110), (202), (220), (310), (224), (134) and (404), respectively [19-20]. This pattern confirms that perovskite was formed with tetragonal crystal structure. However, a peak at 12.7° originated from PbI₂ peak is still observed. It shows that PbI₂ was not fully converted into perovskite CH₃NH₃PbI₃. We presumed it was caused by lack of temperature control during spin-coating process. The film should be gradually cooled to room temperature to give a time for crystal growing.

In variation-2, we used the parameters in literature [21], due to similar materials that used in our experiment. A significant different XRD pattern was observed in perovskite film variation-2 as compared to variation-1. Only five main peaks are observed at 14.2°, 28.5°, 31.8°, 40.5°, and at 44.0° which correlated to the crystal orientation at (110), (220), (310), (224), and (134), respectively. Two peaks at 12.7°, and 28.5° are much higher intensity as compared to other peaks, which shows that perovskite crystal variation-2 is mainly oriented at x-y axis. Moreover, no peak originated from PbI₂ is observed. It shows that all PbI₂ is fully converted to perovskite CH₃NH₃PbI₃ crystal.

XRD pattern of perovskite variation-3 shows similar pattern as variation-1, except no peak at 12.7° is observed. It shows that spin-coating of PbI₂ and MAI solutions at room temperature can obtain fully perovskite crystal. Room temperature spin-coating process is more preferable for large area and mass production and also easier spin-coating control process of perovskite film.
Figure 1. XRD pattern of PbI$_2$, and perovskite films prepared with different spin-coating parameters

Figure 2. SEM photographs of PbI$_2$ films spin-coated at 70°C (left) and at room temperature (right)

SEM of PbI$_2$ films prepared at 70°C and at room temperature are shown in Figure 2. Both pictures show similar fibril or needle-like structure which means that no significant difference of PbI$_2$ crystal spin-coated from homogeneous solution at 70°C or at room temperature. It means that spin-coating method at room temperature can be used for standard preparation of high quality PbI$_2$ film.
Figure 3. SEM of perovskite films prepared with different spin-coating parameters. (a). Variation-1, (b). Variation-2, and (c). Variation-3.

Figure 3 shows SEM images of perovskite films with different magnification prepared by using two-step spin-coating method with different spin-coating parameters and different treatment after spin-coating. Needle-like of PbI$_2$ structures are still clearly observed in the film. It confirmed that PbI$_2$ was not fully converted into perovskite as approved from PbI$_2$ peak in XRD pattern as discussed above. Incomplete conversion of PbI$_2$ into perovskite lead to large hysteresis of J-V curve and low PCE in
perovskite solar cells [22]. Small grain size of perovskite crystal with average size of 200 nm is obtained and also some pin-holes or voids between grains of perovskite are still clearly observed. These pin-holes must be reduced to avoid direct contact of other layers deposited onto perovskite film which lead to inferior performance and large hysteresis in J-V curve of perovskite solar cells [23].

In case of perovskite variation-2, large empty spaces between perovskite grains or clusters are clearly observed. It might be caused by too high of spinning speed of spin-coated PbI₂ and MAI. Although, PbI₂ was fully converted into perovskite crystal as shown in its XRD pattern, this perovskite film is not suitable for perovskite solar cells due to large pin-holes between perovskite crystals.

In contrast, small and only few pin-holes are observed in perovskite film variation-3. Moreover large grain size of perovskite crystal with average size above 500 nm is obtained by spin-coating parameter of 1000 rpm for 20 seconds and at room temperature. Therefore, we recommend these parameters can be used as standard parameters of two-step spin-coating method in air with high humidity for preparing high quality perovskite film with pin-hole free and large grain size to obtain high performance of perovskite solar cells.

Recent study of Cohen et al [23] shows that pin-hole free of perovskite film can produce high PCE perovskite solar cells with reduced hysteresis, due to small series resistance of devices and reduced charge carrier recombination in active layer of solar cells. Kim & Park [24] and Kim et al [25] studied perovskite solar cells with different grains size of perovskite. They found that the PCE of solar cells is improved when grains crystal size is also improved from 100 nm to 500 nm. The improvement of PCE with increasing of grain size is caused by the increased of External Quantum Efficiency (EQE) at longer wavelengths which related to negligible losses in the charge generation and collection in solar cells with large perovskite grains size [25]. The same trend was also found in the absorption spectra measured in the reflectance mode. They found that the photocurrent improvement is primarily attributed to the enhanced absorption due to the thicker active layer with larger perovskite crystal grains size [25].

4. Conclusion
We have prepared perovskite films using two-step spin-coating method with different parameters. Pin-hole free and large crystal size above 500 nm was obtained at low spinning-speed at 1000 rpm and at room temperature spin-coating process. These parameters can be used as a standard process of two-step spin-coating method in air with high humidity (> 80%) for producing high crystal quality with large grains size perovskite films.

Acknowledgments
This work was financially supported by International Collaboration and Scientific Publication Grant from Ministry of Research, Technology and Higher Education (Kemenristekdikti), Contract No. 431/UN6.3.1/PL/2016 dated on February 19, 2016.

References
[1] http://www.nrel.gov/ncpv/images/efficiency_chart.jpg (accessed on September 25, 2016).
[2] Baikie T, Fang Y, Kadro J M, Schreyer M, Wei F, Mhaisalkar S G, Grätzel M and White T J 2013 J. Mater. Chem. A. 1 5628.
[3] Brettscheider S A, Weickert J, Dorman J A and Schmidt-Mende L 2014 App. Phys. Lett. 2 040701.
[4] Hao F, Stoumpos C C, Cao D H, Chang R P H and Kanatzidis M G 2014 Nat. Photon. 8 489.
[5] Noel N K, Stranks S D, Abate A, Wehrenfennig C, Guarnera S, Haghighirad A A, Sadhanala A, Eperson G E, Johnston M B, Petrozza A M, Herz L M and Snaith H J 2014 Energy Environ. Sci. 7 3061.
[6] Kojima A, Teshima K, Shirai Y and Miyasaka T 2009 J. Am. Chem. Soc. 131 6050.
[7] Boix P P, Nomomura K, Mathews N and Mhaisalkar S G 2014 Materials Today 17 16.
[8] Wang B, Xiao X and Chen T 2014 Nanoscale 6 12287.
[9] Kim H S, Im S H and Park N G 2014 J. Phys. Chem. C. 118 5615.
[10] Green M A, Ho-Baillie A and Snaith H J 2014 Nat. Photon. 8 506.
[11] Lee M M, Teuscher J, Miyasaka T, Murakami T N and Snaith H J 2012 Science 338 643.
[12] Eperon G E, Burlakov V M, Docampo P, Goriely A and Snaith H J 2014 Adv. Funct. Mater. 24 151.
[13] Burschka J, Pellet N, Moon S J, Humphry-Baker R, Gao P, Nazeeruddin M K and Grätzel M 2013 Nature 499 316.
[14] Zhou H, Chen Q, Li G, Luo S, Song T, Duan H S, Hong Z, You J, Liu Y and Yang Y 2014 Science 345 542.
[15] Bi D, Yi C, Luo J, Décoppet J D, Zhang F, Zakeeruddin S M, Li X, Hagfeldt A and Grätzel M 2016 Nat. Energy (in press), DOI: 10.1038/ENERGY.2016.142.
[16] Zhang W, Saliba M, Moore D T, Pathak S K, Hö rantner M T, Stergiopoulos T, Stranks S D, Eperon G E, Alexander-Webber J A, Abate A, Sadhanala A, Yao S, Chen Y, Friend R H, Estroff L A, Wiesner U and Snaith H J 2015 Nat Commun. 6 6142.
[17] Chang C Y, Chu C Y, Huang Y C, Huang C W, Chang S Y, Chen C A, Chao C Y and Su W F 2015 ACS Appl. Mater. Interfaces 7 4955.
[18] Cohen B E and Etgar L 2016, Front. Optoelectron. 9 44.
[19] Cao D H, Stoumpos C C, Malliakas C D, Katz M J, Farha O K, Hupp J T, Kanatzidis M G 2014 APL Mater. 2, 091101.
[20] Zheng E, Wang X F, Song J, Yan L, Tian W, Miyasaka T 2015 ACS Appl. Mater. Interfaces 7 18156.
[21] Shao Y, Xiao Z, Bi C, Yuan Y, Huang J 2014 Nat Commun. 5 5784.
[22] Jacobsson T J, Baena J P C, Anaraki E H, Philippe B, Stranks S D, Bouduban M E F, Tress W, Schenk K, Teuscher J, Moser J E, Rensmo H, Hagfeldt A 2016 J. Am. Chem. Soc. 138 10331.
[23] Cohen B E, Aharon S, Dymshits A and Etgar L 2016, J. Phys. Chem. C 120 142.
[24] Kim H S and Park N G 2014 J. Phys. Chem. Lett. 5 2927.
[25] Kim H D, Ohkita H, Benten H, Itó S 2016 Adv. Mater. 28 917.