Influences of Precursor Solution Concentration and Temperature on CH$_3$NH$_3$PbI$_3$ Perovskite Layer Morphology and the Unconverted PbI$_2$ Proportion to their Perovskite Solar Cell Characteristics

Mhd. Ikhsan Alturisa$^1$, Joe Wira$^1$, Mardiyati$^1$, Herman$^2$ and Rahmat Hidayat$^2$

$^1$Materials Engineering Program Study, Faculty of Mechanical and Aerospace Engineering, Institut Teknologi Bandung, Indonesia
$^2$Physics of Magnetism and Photonics Research Division, Physics Program Study, Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung, Indonesia

e-mail: rahmat@fi.itb.ac.id

Abstract. The formation of organometal-halide perovskite crystal is simply based on stoichiometry reaction. However, the formation process seems to be sensitively affected by some process parameters such as concentration and temperature of precursor solution. In this work, we studied the formation of CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) crystal in mesoporous TiO$_2$ layer deposited by spin coating technique. Perovskite layers were characterized by X-Ray Diffraction (XRD) and its surface morphology were investigated by Scanning Electron Microscope (SEM). Perovskite layers obtained from precursor solution at 40$^\circ$C and 60$^\circ$C show a mesh-like structure. Meanwhile, for higher precursor solution temperature (80$^\circ$C), it shows a flake-like structure. However, precursor solution at 60$^\circ$C produced the best conversion of precursor solution with the smallest percentage of the remaining unconverted PbI$_2$ inside the produced crystal layer. These experimental results also showed that the best crystallization degree is obtained from 1.0 M precursor solution. The photovoltaic characteristics of their solar cells seem to have a correlation with the quantity of unconverted PbI$_2$. High PbI$_2$ content significantly decreased the Filling Factor of the solar cell.

1. Introduction

Research in the application of organometal-halide perovskite (hybrid perovskite) as an active layer in solar cells has significantly increased in the past 5 years [1,2]. This material exhibits photovoltaic characteristics with relatively small energy gap [3], and therefore becomes a good candidate for active layer in solar cell. Despite of its simplicity in its preparation, this hybrid perovskite material produced remarkable high solar cell efficiency. The key feature of this material is that it can be synthesized with wet-chemical process at low temperature. This low temperature process feature could reduce the cost of cell fabrication which leads to open a possibility of much cheaper solar cell among the third generation of solar cells.

Research works on hybrid perovskite material as an active layer in a solar cell were pioneered by Miyasaka and co-workers in 2009 [4]. The best efficiency of this perovskite solar cell (PSC) was just 3.81% at that time. However, in just 5 years since that report, the PSCs efficiency records increased significantly up to 20.1% [5]. The most studied hybrid perovskite material in PSC is methylammonium...
lead iodide (CH$_3$NH$_3$PbI$_3$ or MAPbI$_3$). Thin film perovskite layer is commonly deposited onto a substrate using spin coating technique from precursor solution, which is prepared by dissolving lead halide salt and organic halide salt powders at a specific mole ratio in a high boiling point aprotic polar solvent [6]. Commonly, a mesoporous substrate, for instance from TiO$_2$, is used as the substrate.

The formation of MAPbI$_3$ crystal is given by the following reaction scheme:

$$\text{PbI}_2 + \text{MAI} \rightarrow \text{MAPbI}_3,$$

which is a reaction with simple reaction stoichiometry. The formed crystal is believed to be formed by ionic bond. However, weak interaction such as a Coulomb force, which works in two opposite charges, may also contribute in this crystal formation. The reaction rate is very fast but the reaction seems to be highly sensitive with some reaction parameters such as precursor concentration, air humidity and processing temperature. Those parameters seem to affect the conversion degree from precursor solution to crystal perovskite layer. Therefore, the formed perovskite crystal layer from this reaction may also include the unreacted PbI$_2$, which affect the solar cell performance [7]. PbI$_2$ has poor electrical conductivity and higher conduction band than perovskite, which may prevent electron injection to TiO$_2$ and provide charge carrier transport channel with Ohmic characteristics. In the research work reported here, we investigated the effect of preparation parameters from precursor solution (i.e. temperature and concentration) in one-step solution process on the formed perovskite crystal layer characteristics and their solar cell performances.

2. Experimental

2.1. Substrate preparations and MAPbI$_3$ layer formation
Flourine-doped Tin Oxide (FTO)-coated glass (TCO22-7, Solaronix) was used as the solar cell substrate. This FTO substrate was cut into small pieces with size around 2.5 × 2.5 cm$^2$. Each substrate was etched with HCl and zinc powder to form a strip-like electrode pattern. The patterned substrates were then cleaned by sonication in washing liquids consecutively, namely Teepol solution, aqua DM, acetone and ethanol, for 5 minutes in each liquid. After being cleaned, the substrates were dried with air gun. A compact-TiO$_2$ (c-TiO$_2$) precursor solution (Ti-nanoxide BL/SC, Solaronix) was spin-coated onto the substrate at 5000 rpm for 30 s and then followed by sintering at 550°C for 1 hour. After c-TiO$_2$ deposition, the substrates were then coated with mesoporous-TiO$_2$ (m-TiO$_2$) by spin coating technique at 5000 rpm (acc. 2000 rpm/s) for 30 s from diluted m-TiO$_2$ precursor solution (Ti-nanoxide T/600SC, Solaronix) with ethanol (Sigma-Aldrich) at volume ratio 1:1. After spin coating, those TiO$_2$ coated substrates were sintered at 475°C for 30 minutes.

Perovskite precursor solutions were made by dissolving equimolar mixture of PbI$_2$ (Sigma-Aldrich) and MAI (Luminescence Tech.) in DMF (Sigma-Aldrich). Precursors were made into two concentrations: 0.5 M (PSX-C05 sample) and 1.0 M (PSX-C10 sample). Precursor solutions were heated up to 120°C for 20 minutes to promote complete dissolution of PbI$_2$ [8]. Perovskite solution with 1.0 M concentration was also used for producing samples for studying the temperature effect. The precursor solution temperature prior to spin coating were set to 40°C (PSX-T40 sample), 60°C (PSX-T60 sample), and 80°C (PSX-T80 sample). The precursor solutions were then spin-coated at 3000 rpm for 30 s and heated at 90°C for 90 minutes. For producing samples for studying the effect of precursor solution concentration, all precursor solutions prior to spin coating were set at 60°C. These perovskite layers were made inside a glove-box with nitrogen atmosphere to minimize the effect of moisture and oxygen.
2.2. Perovskite solar cell fabrication

After the deposition of active layer, the next process is the deposition of hole transport material (HTM) and gold (Au) electrode. HTM solution was deposited by spin coating at 5000 rpm for 30 s, which was prepared by dissolving 72.3 mg of Spiro-OMeTAD (Luminescence Tech.) in 1 ml chlorobenzene. Additional substances were added to this HTM solution to improve the conductivity of the formed layer, namely 27 µl of FK 102 Co (III) TFSI (Co[PyPz]₃[TFSI]₃) solution (with concentration of 300 mg/ml acetonitrile) and 20 µl of Lithium bis(trifluoromethanesulfonimidate) (LiTFSI) solution (with concentration of 455 mg/ml acetonitrile). After the HTM layer deposition, the substrates were left overnight inside the glovebox to let oxidization process in the HTM layer. Finally, 80 nm of gold (Au) layer was thermally evaporated on the HTM layer to form the back electrode contact. In order to prevent direct contact with moisture and oxygen in air atmosphere during the solar cell characterizations, each cell was covered with sodalime glass and sealed with epoxy adhesive. Figure 1 shows a PSC sample and its structure. PSC samples for studying the effect of precursor solution concentration were named as PSC-05 (for 0.5 M precursor concentration) and PSC-10 (for 1.0 M precursor concentration).

![Figure 1. Perovskite solar cell (a) and its structure (b).](image_url)

2.3. MAPbI₃ thin films characterizations

Each perovskite layer was characterized by scanning electron microscopy (SEM JEOL 6030 LA) to see the morphology of the formed crystal layer. In order to evaluate the perovskite crystal formation, XRD measurements were conducted by using a Bruker D8 Advanced X-ray Diffractometer with Kα Cu as the X-Ray source. Step size of 0.02 degree and an acquisition time of 2 s/degree were chosen in the measurement setup. The measured XRD patterns were analyzed using Match! ver. 3.0 software and Crystallography Open Database (COD) ver. 20150706 as reference library.

2.4. Perovskite solar cell (PSC) characterization

The measurements of J-V characteristic of PSC samples were performed by using Oriel Sol 3A™ solar simulator (Newport) that was connected with a digital sourcemeter Keithley 2400. The cell was illuminated under 1 sun (intensity: 100mW/cm²) with active area of 0.25 cm². Forward bias voltage from -0.2 V to 1.0 V was applied to the cell during the measurement.

3. Results and discussion

3.1. Influence of precursor solution temperature

Figure 2 shows the XRD patterns of MAPbI₃ perovskite layer spin-coated at various temperatures. XRD pattern with COD entry no. 96-433-5369, which is based on the publication by Stoumpos et al.
[9], was used as a reference. XRD peaks from MAPbI$_3$ perovskite crystal are denoted with letter “P” along with its Miller indices. These XRD peaks are in good agreement with literatures. The most intense peak is at 14.1°, which indicates the diffraction from (110) and (002) planes. The presence of small peaks at 23.5° and 30.1° indicates the diffraction from (211) and (213) planes, which belongs to β-MAPbI$_3$ phase [3,10]. The β-phase is phase of MAPbI$_3$ that presents in room temperature.

Figure 2. XRD patterns of MAPbI$_3$ spin-coated at 40°C (PSX-40 sample), 60°C (PSX-60 sample), and 80°C (PSX-80 sample).

In addition to peaks originated from the perovskite crystal, there is also a peak which does not belong to perovskite crystal. A peak (denoted with letter “L”) observed at $2\theta = 12.65°$ is the diffraction peak from (001) plane of PbI$_2$ [11]. The presence of this L-peak in all XRD patterns shows that there is a small amount of unconverted PbI$_2$ left in perovskite films. As the precursor solution temperature increasing from 40°C, 60°C to 80°C, there is a decrease in L-peak’s intensity from 4967 cps, 4738, and 4402 cps. Table 1 shows the percentages of PbI$_2$ in perovskite layer made at various precursor solution temperatures. As the temperature increasing from 40°C to 60°C, the PbI$_2$ content in perovskite decreases from 4.70% to 3.97%. However, when the temperature is increased from 60°C to 80°C, there was an increment in PbI$_2$ percentage.

Table 1. PbI$_2$ contents in MAPbI$_3$ perovskite layer (based on Match! Software calculation).

| No. | Precursor temperature | PbI$_2$ content in perovskite |
|-----|-----------------------|------------------------------|
| 1   | 40 °C                 | 4.70%                        |
| 2   | 60 °C                 | 3.97%                        |
| 3   | 80 °C                 | 9.74%                        |

These results may be related with better PbI$_2$ solubility at higher temperature, which is related to the increment of (110) and (002) peak intensity from 19,589 cps to 24,555 cps for an increase of precursor temperature from 40°C to 60°C. However, the same peak intensity from sample of 80°C is just 10,366 cps, which may indicate much thinner layer due to higher viscosity of precursor solution at this temperature.
Figure 3 shows the SEM images of perovskite layer surface which were prepared at various temperatures. Perovskite layers spin-coated from precursor solution with temperature at 40°C and 60°C have a mesh-like crystal structure. The perovskite crystals tend to grow at one direction, as in agreement with their XRD patterns that exhibit one intense peak at 14.1°.

(a) (b) (c)

**Figure 3.** SEM images of perovskite layers spin-coated at (a) 40°C, (b) 60°C, and (c) 80°C.

On the contrary, perovskite layer spin-coated from precursor solution with temperature at 80°C have flake-like morphology, which may indicate higher dimensionality of crystal structure. This shape explains why the XRD pattern of sample PSX-T80 exhibits several intense peaks from lattice plane with larger Miller indices. However, PSX-T80 shows uncovered surface area that may cause a problem on the cell performance.

3.2. Influence of precursor concentration on perovskite crystal formation

![XRD patterns](image)

**Figure 4.** XRD patterns of perovskite layer spin-coated from precursor solution with concentration of (a) 0.5 M (PSX-C05 sample) and (b) 1.0 M (PSX-C10 sample).

Figure 4 shows the XRD patterns of perovskite layer samples. In the patterns, a peak appeared at 37.9° which belongs to the diffraction from (200) plane of FTO and (004) plane of TiO₂ anatase phase. The appearance of this peak might be happen if the perovskite layer was very thin compared to the X-ray penetration depth.
As the precursor solution concentration was decreased from 1.0 M to 0.5 M, the intensity of (110) peak at 14.1° also decreases but the PbI$_2$ peak increases. The PbI$_2$ content in PSX-C05 sample and PSX-C10 sample are estimated to be about 5.71% and ~0.1%. PSX-C05 sample has brown color, while PSX-C10 has black color. Nevertheless, both samples show brown color if viewed in transmittance mode. The observation of high PbI$_2$ content in low concentration of precursor solution may be explained as follows. Precursor solution with lower concentration contains more solvent than the higher concentration one. With the same volume of precursor solution dispensed onto the substrate and the same spinning rate of spin coating process, solvent in low concentration precursor will evaporate slower than the high concentration precursor. Delaying solvent evaporation would give enough time for PbI$_2$ to crystallize as the temperature drops. Therefore, precursor with 1.0 M concentration is better than precursor with 0.5 M concentration because it has higher conversion to perovskite crystals.

3.3. Solar cell performance

Figure 5 shows the J-V curves of PSC where the precursor solution was set at 60°C. PSC samples made from precursor with concentration of 0.5 M (PSC-05 sample) and 1.0 M (PSC-10 sample) exhibit power conversion efficiency of 4.65% and 4.34%. As the precursor concentration was decreased from 1.0 M to 0.5 M, there is an increment in efficiency, $J_{sc}$, and $V_{oc}$ by 0.31%, 1.83 mA/cm$^2$ and 0.22 V, respectively. The Filling Factor (FF) value seems, however, not good enough. This may be due to the presence of uncovered mesoporous TiO$_2$ regions and unconverted PbI$_2$, where it becomes Ohmic and recombination sites during the J-V curve measurement. For PSC made by 1.0 M precursor concentration, the precursor might be viscous enough so that the solution rather difficult to penetrate TiO$_2$ pores. Therefore, the perovskite crystals are dominantly deposited on the surface of mesoporous TiO$_2$ layer. This condition would prolong electrons paths to travel to from photo-excited perovskite to FTO layer and increase the recombination rate, but that condition creates more perfect junction structure. A solar cell having perfect junction structure would have high FF value, which is also necessary in order to convert photon into electricity efficiently.

4. Conclusion

The present experimental result shows how the precursor solution parameters, i.e. its temperature and concentration, in one-step solution process affect the formed perovskite crystal characteristics and also
the fabricated PSC. The temperature of precursor solution affects the formed perovskite layer crystallinity and morphology as well as the unconverted PbI$_2$ amount. Perovskite layers made by spin coating precursor at 40°C and 60°C produce a mesh-like structure, while the layer at higher precursor temperature (80°C) produce a flake-like structure. In this work, perovskite layer with the smallest PbI$_2$ content was obtained using precursor solution temperature at 60°C. At low precursor concentration (0.5 M), the amount of unconverted PbI$_2$ increases up to 5.71%. Those formed perovskite layer has influence on their PSC characteristics indicated by their J-V curves. Although PSC made from 0.5 M precursor concentration has slightly higher efficiency, $J_{sc}$, and $V_{oc}$, but it has bad FF value. This may be due to imperfect mesh-like structure with considerable amount of uncovered TiO$_2$ region and unconverted PbI$_2$. PSC from precursor with 1 M precursor concentration shows much better FF value that indicates the formation of better junction structure. Although the perovskite crystals are more deposited on the top of the mesoporous TiO$_2$ layer, rather inside its pores, the formation of junction structure seems better in this case.

Acknowledgements
Authors are very grateful for the kindness of Prof. M Okazaki of Osaka University and his laboratory members for using their experimental facilities during our research visit. This research was supported by Program Hibah Kerjasama Luar Negeri 2015/2016 from DIKTI.

References
[1] Chen Q, Marco N D, Yang Y M, Song T, Chen C, Zhao H, Hong Z, Zhou H and Yang Y 2015 J. Nanotod. 10 355-396
[2] Snaith H J 2013 J. Phys. Chem. Lett. 4 3623–30
[3] Baikie T, Fang Y, Kadro J M, Schreyer M, Wei F, Mhaisalkar S G, Graetzel M and White T J 2013 J. Mater. Chem. A 1 5628–41
[4] Kojima A, Teshima J, Shirai Y and Miyasaka T 2009 J. Am. Chem. Soc. 131 6050–51
[5] NREL 2015 Research Cell Efficiency Records. http://www.nrel.gov/ncpv/images/efficiency chart.jpg
[6] Gao P, Graetzel M and Nazeeruddin M K 2014 J. Energy Environ. Sci. 7 2448–63
[7] Cao D H, Stoumpos C C, Malliakas C D, Katz M J, Farha O K, Hupp J T, and Kanatzidis M G 2014 APL Mater. 2 091101; doi: 10.1063/1.4895038
[8] Bi D, El-Zhory A M, Hagfeldt A and Boschloo G 2015 ACS Photonics 2 589–94
[9] Stoumpos C C, Malliakas C D and Kanatzidis M G 2013 Inorg. Chem. 52 9019–38
[10] Song Z, Watthage S C, Phillips A B, Tompkins B L, Ellingson R J and Heben M J 2015 27 4612–19
[11] Khatiwada D, Vankatesan S, Adhikari N, Dubey A, Mitul A F, Mohammad L, Iefanova A, Darling S B and Qiao Q 2015 J. Phys. Chem. C 119 25747–53