The Influence of Humid Atmosphere during the MAPbI₃ Perovskite Layer Preparation on the Characteristics of Its Solar Cells

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Abstract. Organometal halide perovskite (hybrid perovskite) materials have emerged as a promising material for high power conversion efficiency and low-cost solar cells. The formation of organo-metal halide perovskite layer, however, is very sensitive to some process parameters such as concentration, temperature, and humidity. In this study, we report the preparation of CHNH₃PbI₃ (MAPbI₃) perovskite crystal layers under a relatively humid air atmosphere and investigated the characteristics of their solar cells with both mesoporous cell structure and planar cell structure. Due to high humidity, we found that the formed layer tends to form a shiny grey to black color layer on the top of the dark brown color perovskite layer. This layer showed poor x-ray diffraction (XRD) pattern and caused poor solar cell performance. The formation of this layer, however, can be prevented by anti-solvent treatment during the preparation of perovskite layer.

1. Introduction

Recently organic–inorganic metal halide perovskite (OMHP) have been rapidly studied as an absorber in solar cells. Perovskite with ABX₃ formula (A = CH₃NH₃, B = Pb or Sn, X = I, Br or Cl) were discovered in 1978 [1]. The first report of perovskite application in solar cells reported by Kojima and colleagues exhibit 3.8% by using DSSC structure [2]. In 2012, two different research groups, namely Snaith and Gratzel groups, reported higher power conversion efficiency (PCE) around 10% at their first attempts [3,4,5,6]. Different form metal oxide perovskite, these halide-based perovskites shows semiconductor material properties and exhibits photovoltaic characteristics. These halide based perovskite shows unique properties such as high absorption coefficient, long hole-electron diffusion length, tunable band gap, and good carrier transport.

Recently, the power conversion efficiency (PCE) has increased to 22.1% reported by Yang et al [7]. High PCE of solar cells needs perovskite film with a smooth surface, large grain size, and full surface coverage. To date, one step precursor deposition (OSPD) of the perovskite layer is one of the fastest and most cost-effective processes. However, the formation and stability of perovskite crystal are strongly influenced by such as oxygen, humidity, temperature, and solvent type. Morphology and crystal structure of perovskite films changed upon exposure to a high relative humidity environment (80%). The appearance of monohydrate coincides with additional grain boundaries. Prolong exposure time to humidity caused more grain boundaries and step in perovskite films and monohydrate [8]. Xiao et al. have reported that the OSPD method modified with anti-solvent treatment to induce fast
crystallization-deposition (FDC) could produce a flat and highly uniform CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} thin film. This OSPD+FDC method offers the advantage of single-step processing and short deposition times as the film formation can be completed within 1 min [9]. It is therefore interesting to explore this method for preparing MAPbI\textsubscript{3} perovskite crystal layers under humid air atmosphere, which is a common condition in tropical countries, and understanding the influence of the resulted perovskite layer characteristics on the performance of their solar cells.

2. Experimental

In this study, perovskite solar cells with mesoporous and planar structures have been fabricated. The perovskite layers prepared by OSPD and OSPD+FDC techniques. Firstly, mesoporous structure which consist of six layers (FTO/c-TiO\textsubscript{2}/mp-TiO\textsubscript{2}(ETL)/CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}/PT(HTL)/Au and planar structure composed by ITO/PEDOT:PSS(HTL)/CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}/PCBM(ETL)/Ag. Each layer was made by different methods. For planar structure, PEDOT:PSS was spin-coated on ITO substrate at 1000 rpm for 30 s and annealed at 110°C for 10 min. The perovskite solutions made by dissolving 0.461 g PbI\textsubscript{2} in DMF and DMSO (vol ratio = 1:1) and 0.159 g MAI was added when the PbI\textsubscript{2} was already dissolved. The perovskite layers prepared by OSPD+FDC method on ITO/PEDOT:PSS at 5000 rpm using diethyl ether as antisolvent in a glovebox with air humidity of 30%-60%. After spin coating, these perovskite layers were annealed at 90 °C. PCBM as an ETL was spin coated on ITO/PEDOT:PSS/CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} at 1500 rpm for 30 s. Finally, 100 nm Ag electrode was deposited by thermal evaporation.

Mesoporous structure of perovskite solar cell fabricated by deposit compact and mesoporous TiO\textsubscript{2} layer on a pre-cleaned FTO substrate by spin coating technique at 5000 rpm for 30 s as reported in our previous studies, but the thicknesses of the layers were much thinner than the previous reports [10,11]. After the spin coating process, those TiO\textsubscript{2} layers were annealed sequentially at 100°C for 15 min, 300°C for 15 min and 500°C for 30 min. The perovskite layers were then prepared either by the simple OSPD method or the OSPD+FDC method. The perovskite precursor solution was made from 0.922 g of PbI\textsubscript{2} and 0.318 g MAI in 1 ml DMF:DMSO in a glovebox with air humidity of 30%-60%. This perovskite precursor solution was spin coated onto the mesoporous TiO\textsubscript{2} layer (with the structure of FTO/c-TiO\textsubscript{2}/m-TiO\textsubscript{2}) by spin coating at 5000 rpm for 30 s. Ethyl acetate was used as the antisolvent. After the spin coating, the film was annealed at 90°C for 60 min. For constructing a complete solar cell, the hole transport layer and Au electrode were sequentially deposited on the top of the perovskite layer. The resulted perovskite layers in this work were characterized by absorption (UV-Vis) spectroscopy, Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) measurements.

3. Result and Discussion

![Figure 1](image1.png)

Figure 1. SEM images of the CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} layer prepared on the top of (a) TiO\textsubscript{2} (by OSPD technique) (b) TiO\textsubscript{2} (by OSPD+FDC technique) (c) PEDOT:PSS (by OSPD+FDC technique) layer.

Figure 1 shows SEM images of the CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} perovskite layer surface prepared by OSPD and OSPD+FDC. Analysis of layers by SEM revealed strikingly different morphologies. Figure 1(a) SEM
images of perovskite layer produced by OSPD method in this humid air condition looks like a resemble of random needle-like shapes or an overlapping web, which is similar as reported previously [9]. It can also be seen easily the presence of the areas on the layer that are not covered by the perovskite crystals. The formation of needle-like shapes seems more favorable in the humid air because such morphology was not found in samples prepared in dry air atmosphere as reported in literature elsewhere [12]. On the other hand, flake-like layers with dark brown color have been obtained by the OSPD+FDC method. It shows a full coverage surface film. The addition of anti-solvent onto the spinning wet films to initiate nucleation and crystal growth after delay times from the start of spinning. All of the spinning process divided into three stages. At the first five seconds of spinning (the stage 1), the removal of the excess precursor solution is a dominant process. In the stage 2 (5-10s), the evaporation of the residue solvent occurs significantly concentrating the perovskite solution from which a dense and uniform film was formed when the anti-solvent was introduced. In the stage 3 (after 10 s), the film started to dry and become solid.

Figure 2. Absorption spectra of CH₃NH₃PbI₃ layer prepared by OSPD and OSPD+FDC methods

Figure 2 shows the plots of the absorption spectra of the perovskite layers. The absorption of CH₃NH₃PbI₃ (-FDC) layer, that was prepared without anti-solvent treatment, shows a spectrum broadens up to the near infra-red region (up to 1100 nm). On the other hand, the OSPD+FDC layers, that were prepared with the anti-solvent treatment, seem to be less affected by the air humidity. Under perfect process handling, even in humid air condition, a dark brown color perovskite layer covering the entire surface of TiO₂ layer can be eventually obtained. This is indicated by the cut off of its absorption spectrum at about 780 nm, as indicated in Figure 2. The dark brown layer was also observed in the perovskite layer prepared on the top of PEDOT:PSS, as depicted in Figure 2. Its absorption spectrum also shows a cut off at 780 nm. This FDC process or anti-solvent treatment can effectively reduce the formation of shiny gray to black color particles on the layer surface.
Figure 3. XRD pattern of CH$_3$NH$_3$PbI$_3$ perovskite layer prepared by (a) OSPD and (b) OSPD+FDC

Figure 3(a) shows the XRD patterns of the CH$_3$NH$_3$PbI$_3$ layer prepared by OSPD which has shiny-gray to black color. The spectrum shows some peaks at low intensity with a broad background indicating a dominant amorphous phase. In contrast, Figure 3(b) shows XRD pattern of CH$_3$NH$_3$PbI$_3$ layer prepared by OSPD+FDC that reveals some peaks with high intensity at the position of 14.10°, 19.95°, 23.48°, 28.43°, 31.87°, 40.63°, 43.25° which can be assigned to (110), (112), (121), (220), (201), (121), (224) and (006) crystal planes of the CH$_3$NH$_3$PbI$_3$ perovskite. Compared to these XRD peaks, the XRD pattern for the first CH$_3$NH$_3$PbI$_3$ layer, then indicates that the shiny-gray to black color layer contains dominantly an amorphous phase or non-crystalline structure with a small quantity of non-perovskite crystal.

Figure 4. J-V curve of PSC with the perovskite layer prepared by the OSPD method

Figure 4 shows the J-V curve of this perovskite solar cell (PSC) with the perovskite layer prepared by the OSPD method. This cell exhibits a poor J-V curve mainly because of cell shunting or high electron-hole recombination. In other words, the photogenerated electrons and holes suffer high recombination, which likely occurs at the interface or inside this shiny grey to black color layer.
Figure 5. J-V curves of PSC with the perovskite layer prepared by OSPD+FDC method on the top of (a) TiO$_2$ layer (b) PEDOT:PSS layer.

Figure 5 shows the plots of the J-V curve of these PSCs with the perovskite layer prepared by the OSPD+FDC method. Both PSCs, either made by mesoporous structure or planar structure, shows better solar cell characteristics. As shown in Figure 5(a), the PSC with mesoporous structure exhibited a good working performance as indicated by a high $J_{SC}$ of 16.6% and PCE of around 8.0%. For the planar structure, as shown in Figure 5(b), this PSC cell yielded $J_{SC}$ of 10.2 mA/cm$^2$ and PCE of 4.8%. These characteristics are related to the formation of the flake-like perovskite domain and less charge carrier recombination due to the absence of the shiny greyish to brown color layer.

4. Summary
The one-step precursor deposition (OSPD) followed by fast deposition crystallization (FDC) technique seems able to reduce the effect of humidity. The humid air seems to promote the formation of shiny greyish to black color layer and needle-like crystal shape. The perovskite layer made only by the OSPD technique yielded a poor solar cell performance. The perovskite layer made by the OSPD+FDC technique may produce a much better solar cell performance for PSCs either with the mesoporous structure or the planar structure.

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