Growth of CH$_3$NH$_3$PbI$_3$ Perovskite on Stainless Steel Substrate Layered by ZnO Nanoparticles Using One-Step Spin Coating Route

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Abstract: In this work, we report the preparation of CH$_3$NH$_3$PbI$_3$ perovskite using one-step spin coating route for solar cell application. CH$_3$NH$_3$I•PbI$_2$•DMF•DMSO complexes were coated on stainless steel as a subtrate layered by ZnO nanoparticles as an electron transport layer. To obtain samples with a special performance, we annealed the samples at a temperature of 100, 120, and 140 °C for 10 minutes. The samples were then characterized by means of XRD, SEM/EDX, and Spectroscopic Ellipsometry. The analysis of XRD data presented that the CH$_3$NH$_3$PbI$_3$ perovskites were successfully prepared and crystallized in tetragonal structure confirming from crystalline planes (110) and (220). Meanwhile, the particle size of the samples prepared at a temperature of 100, 120, and 140 °C presented 42.96, 54.73, and 55.19 nm, respectively with coincide with the SEM images. The results indicated that the increase in temperature during synthesis influenced the particle growth. Furthermore, the characterization using Spectroscopic Ellipsometry exhibited that the CH$_3$NH$_3$PbI$_3$ successfully layered on the substrate sizing nano metric scale that open high opportunity to be applied to solar cells with high performance.

Keywords: CH$_3$NH$_3$PbI$_3$, perovskite, nanoparticle, one-step spin coating, solar cell

1. Introduction

Organometal halide CH$_3$NH$_3$PbX$_3$ (CH$_3$NH$_3^+$ = MA, X=I, Cl or Br) based Perovskite Solar Cells (PSC) become the main promising candidate of photovoltaic tools in the recent years since they have some excellences such as band gap engineering capabilities (~1.5 eV) [1], the high mobility in bringing the charge and the low recombination speed as well as the big absorption power [2,3]. The characteristic absorption and perovskite light sensitivity are at the wave length of 300-800 nm, especially around 500 nm [4]. In 2009, Power Conversion Efficiency (PCE) of PSC increased from 3.8 % [5] to approximately 21% in 2016 [6]. PSC with PCE which is more than 20% consists of n-i-p structure, in which the perovskite functions as intrinsic semiconductor, TiO$_2$ as an electron transport (n-type layer) and Spiro-OMeTAD as a hole transport (p-type layer) [7]. The increase in the efficiency...
of perovskite solar cells is influenced very much by the layer structure [8], chemical composition of perovskite and its fabrication method [9].

In general, there are two methods to make perovskite solution of solar cell namely one step and two steps [10]. Yazdi et al. reported that the perovskite film producing by using one-step method was easier in controlling solution. Furthermore, by giving anti solvent, the perovskite had a good crystal structure and presenting a higher efficiency than that of two steps method [11]. However, PSC efficiency through one step spin coating method is influenced by solvent control, preheating condition, substrate surface condition and annealing temperature [12]. In 2016, Zhu et al. reported that PSC fabrication used one step spin coating method with the variation of the preheating temperature of 40 °C, and 60 °C and the efficiency was 18.64% with the good stability after it was stored for 20 days at the preheating temperature of 40 °C [10]. Although PSC research develops fast, the toxicity, stability, the selection of layer structure type and the size of crystal grain are rarely learned. Therefore, the further study of such topics is needed in PSC development.

In this work, PSC was grown up by using one step spin coating consisting of Stainless steel/ZnO/CH$_3$NH$_3$PbI$_3$ layer. Stainless steel functions as a substrate layer since it is good and resistant to corrosion, heat, and wear out compared to plastic and polymer [13]. For electron transport layer, ZnO was used as the change of TiO$_2$, since the ZnO conductivity is higher than TiO$_2$[14]. CH$_3$NH$_3$PbI$_3$ was used as perovskite material since its fabrication process is relatively easy, its hole mobility is high and its recombination speed is low [15]. Meanwhile, this work did not use the spiro-OmeTAD material because in original form, spiro-OmeTAD has low conductivity so that it still needs dopant and its price is relatively expensive [16]. In this work, solar cell perovskite was fabricated by using one step spin coating method with the variation of annealing temperature to get the proper film texture for PSC by knowing the structure, morphology, and thickness of the CH$_3$NH$_3$PbI$_3$ film.

2. Materials and Methods

2.1 Growth of ZnO Nanoparticles

ZnO Nanoparticles were synthesized by using sol gel spin coating method on a stainless steel substrate. Before using the stainless steel, it was washed with ethanol, acetone, and deionized water in an ultrasonic cleaner. Zinc Acetate Dihydrate (ZnAc) was diluted in ethanol and it was stirred at a temperature of 70 °C. Subsequently, it was added with Monoethanolamine (MEA) into the solution for two hours. The solution was spun on a substrate with the speed of 3000 rpm. The preheating and annealing process was then done at a temperature of 150 °C for 10 minutes and 450 °C for 2 hours.

2.2 Growth of Perovskite Solar Cells

The CH$_3$NH$_3$PbI$_3$ as the PSC film layer was prepared by using one step coating method and the result of the solution was layered on ZnO film. First was making methylammonium iodide (CH$_3$NH$_3$I) powder by mixing hydroiodic acid (HI) with methylamine (CH$_3$NH$_3$). It was continued by mixing the CH$_3$NH$_3$I powder that had been prepared with Dimethylsulfoxide (DMSO) solution and N,N-dimethylformamide (DMF) that was stirred for 25 minutes. The solution resulted in the spin coating on the layer surface of ZnO nanoparticles/stainless steel. The coating process was done through two ways; they were by adding and without adding the anti solvent of anti-solvent diethyl ether. After that, the sample of CH$_3$NH$_3$PbI$_3$ of PSC film was preheated with the face-up position for 30 seconds. Last, the CH$_3$NH$_3$PbI$_3$ PSC film was annealed with the temperature variations of 100, 120 and 140 °C.

2.3 Characterization

The crystal structure of CH$_3$NH$_3$PbI$_3$PSC film was characterized by using X-ray Diffraction (XRD). The morphology of sample surface was characterized by using Scanning Electron Microscopy (SEM), and Ellipsometry Micropack SpecEl 2000 was used to know the thickness of ZnO nanoparticle film layer and CH$_3$NH$_3$PbI$_3$ perovskite in one system.
3. Result and Discussion

The diffraction patterns of CH$_3$NH$_3$PbI$_3$ PSC are presented in Figure 1.

![Diffraction Pattern of CH$_3$NH$_3$PbI$_3$ PSC](image)

**Figure 1.** Diffraction Pattern of CH$_3$NH$_3$PbI$_3$ PSC with the variation of anneal temperature; a) Without anti-solvent at 100 $^\circ$C, and with anti solvent b) 100 $^\circ$C, c) 120 $^\circ$C, d) 140 $^\circ$C

Figure 1a. Shows the diffraction pattern of CH$_3$NH$_3$PbI$_3$ without using anti-solvent indicating that PbI$_2$ phase was more dominant the original CH$_3$NH$_3$PbI$_3$ phase. Actually, the phase that should be formed more dominantly was CH$_3$NH$_3$PbI$_3$. Meanwhile, the sample added with anti-solvent shown in Figure 2b, 2c, and 2d representing that the diffraction peak of CH$_3$NH$_3$PbI$_3$ PSC film with the annealing temperature variation had the strongest diffraction peak at 13.95$^\circ$ and 28.23$^\circ$; this phenomenon was in line with the study conducted by Zhu et al. (2016) indicating that the original compound of CH$_3$NH$_3$PbI$_3$ had been formed with tetragonal crystal structure and group of 14/mcm [17]. There were three other peaks appearing at the angle of 20 12.44$^\circ$, 64.69$^\circ$, dan 81.95$^\circ$. The peak of 12.44$^\circ$ angles was indexed as the PbI$_2$ residue [3], and the other peaks were included in the diffraction peak of stainless steel substrate [18]. Meanwhile, we can see at the diffraction pattern of CH$_3$NH$_3$PbI$_3$ at a temperature 140 $^\circ$C that there was the impurity of PbI$_2$ with the relatively high intensity peak compared to the intensity of the simple at a temperature of 100 and 120 $^\circ$C. This phenomenon was because of the higher the temperature, the anti-solvent would more easily steam so that it changed the crystal phase.

To know further the film crystallinity, the result of XRD diffraction pattern was also analyzed by Scherrer equation to state the size of the crystal grain. The results of the calculation are presented in Table 1.

| Annealing Temperature ($^\circ$C) | FWHM (rad) | Particle Size (nm) |
|----------------------------------|------------|--------------------|
| 100                              | 0.00354    | 42.96              |
| 120                              | 0.00278    | 54.73              |
| 140                              | 0.00275    | 55.20              |

In Table 1, the particle size increased by the decrease in FWHM value. The change of FWHM and the size of crystal grain was due to the growth period as the result of temperature change. The particle size of CH$_3$NH$_3$PbI$_3$ perovskite with the annealing temperature of 100, 120, and 140 $^\circ$C was 42.96, 54.73, and 55.20 nm, respectively. This phenomenon was in line with the study conducted by Zhu et al. (2016) stating that the film crystallinity increased by the reduce of impurity interstitial of CH$_3$NH$_3$PbI$_3$ and the increase in crystal size [17].
The morphology CH$_3$NH$_3$PbI$_3$ PSC film surface sample was characterized by using SEM. The results of SEM with the variation of annealing temperature are shown in Figure 2.

![Figure 2](image)

Figure 2. The SEM result of CH$_3$NH$_3$PbI$_3$ PSC with the variation of annealing temperature: a) 100 °C, b) 120 °C, c) 140 °C

Figure 2 indicates that CH$_3$NH$_3$PbI$_3$ film was grown inhomogeneously over the substrate surface. However, by the increasing temperature, the morphology was more randomized with the high density. The high density of crystal can cause the quality of electrical and optical characteristics of film decrease so that it automatically causes the PCE of solar cell reduces [19].

The thickness of film becomes an important parameter because it can influence in improving light-harvesting properties [17]. The thickness of layer structure of the CH$_3$NH$_3$PbI$_3$ film was characterized by using Ellipsometry Spectroscopy. The characterization results are presented in Table 2.

| Annealing Temperature (°C) | Thickness of ZnO (nm) | Thickness of CH$_3$NH$_3$PbI$_3$ (nm) |
|---------------------------|----------------------|---------------------------------------|
| 100                       | 154.1                | 79                                    |
| 120                       | 155.1                | 79                                    |
| 140                       | 155.5                | 79                                    |

Table 2 shows that the thickness of each sample at an annealing temperature of 100, 120, and 140 °C was similar that was 79 nm, with the thickness of ZnO layer functioning as an electron transport layer was 154.1, 155.1, 155.5 nm, respectively. This case indicates that the change of annealing temperature did not influence the film layer thickness.

4. Conclusion

The CH$_3$NH$_3$PbI$_3$ PSC film that was grown through one step spin coating route had a tetragonal crystal structure. The highest crystal orientation of all samples with the variation of annealing temperature directed to the peak of (110). The crystal grains of CH$_3$NH$_3$PbI$_3$ were in nano size with the good crystallinity and it grew up on the substrate surface of ZnO nanoparticles/stainless steel holistically that had the thickness of nanometer scale. The high annealing temperature caused the crystal grains were formed randomly with the high density. In addition, it also caused the appearance of PbI$_2$ residue and increased the crystal density that became one of the causes of the decrease in solar cell efficiency. Thereby, in this work, it can be concluded that the proper annealing temperature to produce the solar cell with high performance is 100 °C.

Acknowledgements

The authors would like to thank the Kemenristekdikti for providing funding of Hibah Penelitian PPT for AF 2017.

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