Microstructure study of bismuth oxyiodide thin film prepared by SILAR dip coating

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Abstract. Bismuth Oxyiodide (BiOI) has been recognized as a suitable candidate of non-toxic material to replace lead in perovskite solar cells without reducing its performance. BiOI has been synthesized and deposited using modified successive ionic layer adsorption and reaction (SILAR) dip coating method at room temperature on the microscope glass, as a substrate. The microscope glass was dipped consecutively in 0.1M of bismuth(III) nitrate pentahydrate (Bi(NO3)3·.5H2O) diluted in nitric acid (HNO3) and 0.05M of potassium iodide (KI) in 50 ml deionized water. This process has been repeated for 30 times and finally the sample was dripped and dried in air. The sample was annealed at various annealing temperature from 350, 400, 425 and 450°C, for 1 hour. The physical observation, morphological and thickness of BiOI thin films have been characterized using field emission scanning electron microscope (FE-SEM) and surface profiler, respectively. From the physical observation, the as deposited BiOI thin film shows a thick layer with dark orange colour. The colour of the film changed to orange-yellow after annealed at 350°C for 1 hour. It was observed that the film become more yellowish with increasing annealing temperature. SEM images demonstrated that the BiOI thin films have flakes morphology structure with the grain sizes around 1μm. The flakes agglomerates and formed a flower platelet. The agglomeration increased with higher annealing temperature and finally shattered when the BiOI was annealed at 450°C.

1. Introduction

Perovskite solar cells (PSCs) hold advantage compare to other solar cell due to their speedy increment in conversion efficiency, simplicity and low cost processing [1,2]. All current PSCs with high efficiency contain the harmful lead (Pb), raising a serious environmental concern for large scale development. The risk of Pb contained in material will not only a danger to human and living beings, but also dangerous to the environment [3]. In human, lead is harmful to the nervous and reproductive system. Therefore, many researchers have tried to find another way for replacing Pb in the perovskite structure.

Bismuth oxyiodide (BiOI) has been recognized as the electronic structure necessary to replicate Pb-halide perovskite. BiOI is a low-cost and non-toxic material with narrow bandgap, efficient light absorber with high Shockley-Queisser limit [4, 5, 6]. Bismuth-based compound is the Pb-free material which is easy to synthesis, has lower toxicity in comparison to among semiconductor materials [6, 7,
8] and high tolerance in defect [9]. There are many techniques have been reported to grow BiOI thin film. The most challenging part in thin film deposition and solar cell fabrication is control the chemical composition of the material layers, homogeneity of film, film thickness, lattice mismatch, cracks and pinholes formation and existence of defect surface level [9, 10].

BiOI thin film can be deposited using chemical bath deposition (CBD) [11, 12], spin coating technique [13] and modified successive ionic layer adsorption and reaction (SILAR) dip coating [14]. Among all SILAR and CBD are highlighted to be the common methods in BiOI preparation for solar cell application. SILAR will be used for this study because it simplicity and easy, low-cost, stable and most important able to produce a uniform layer. This paper report the deposition of BiOI thin film using SILAR technique under condition parameter that is annealing temperature. BiOI thin film were annealed at various temperatures to study the physical, morphological structure and thickness for each of the temperature.

2. Method
BiOI was synthesized and grown using modified successive ionic layer adsorption and reaction (SILAR) dip coating technique. Two solutions have been prepared prior to the deposition. The first batch is bismuth nitrate pentahydrate (Bi(NO$_3$)$_3$.5H$_2$O) bath. It has been prepared by diluted 0.1 M of bismuth nitrate (Bi(NO$_3$)$_3$) in 0.001 M nitric acid (HNO$_3$) and 100 ml deionized water. This solution is stirred for 3 hours at room temperature. The second bath is Potassium Iodide (KI) bath. It was prepared by diluted the 0.1M of KI in 100 ml deionized water. The substrate used in this experiment is standard microscope glass slide. The deposition process starts by dipping the glass into (Bi(NO$_3$)$_3$.5H$_2$O) bath for 10 s followed by dipped into KI bath for 20 s for chemical reaction and finally dipped into deionized water for 10 s to complete one cycle. This process was repeated for 30 cycles to obtain a uniform BiOI thin film. The process of this deposition is shown in Figure 1. The physical appearance and morphological of BiOI thin film has been studied through naked eye and Scanning Electron Microscope (SEM) whereas the thickness has been characterized using Surface profiler (SP).

![Figure 1: The dipping process of BiOI thin films.](image-url)
3. Result and Discussion

3.1. Physical Observation
The as deposited BiOI thick layer is obtained with dark orange color. After annealing at 350°C and 400°C for 1 hour, the color of thin film changed from dark orange to soft orange color. The color transformed to the pale yellow when the annealing temperature increased up to 450°C. It is also observed that the BiOI layer started to peel off slightly after annealed at 450°C.

![Figure 2: The physical observation of BiOI thin film for as deposited and annealed at 350, 400, 425 and 450°C.](image)

3.2. Scanning Electron Microscopy (SEM) Analysis
Scanning electron microscopy (SEM) was used to study the effect of annealing temperature on the BiOI thin film surface morphology. From this result, it is demonstrated that the as-deposited BiOI thin films has a flakes-sheet morphology structure with the grain size around 1μm. The obtained flakes-sheet shape could be due to the formation of layer through chemical reaction and dipping cycle during the deposition process. BiOI growth can be affected by the acidity of solution which has an impact on the different facet of BiOI [15]. The flakes agglomerates and formed a flower platelet. The agglomeration increased slightly with higher annealing temperature and the flakes were shattered when the BiOI was annealed at 450°C which could be due to the thermal enhancement that initiated the grain growth.
3.3. **Thickness Measurement**

The thickness measurement was carried out using surface profiler. The measurement of each sample was carried out three times at different film areas in order to get an accurate average thickness. Figure 4 shows the graph of the average thickness measurement versus annealing temperatures. It shows that the thickness has reduced slightly from 400 nm (as-deposited) to ~350 nm when it was annealed at 350°C. The thickness shows rapid decline to ~100 nm at a temperature range of 450°C, which is due to the sublimation of material at high temperatures [16]. Therefore, the annealing of BiOI layers in air should be limited to a temperature of 400°C, in order to avoid loss of the material and quality of film.

![Figure 4: Thickness of BiOI thin films as a function of annealing temperatures.](image-url)
4. Conclusion
Thin films of Bismuth oxyiodide (BiOI) were successfully deposited, using dip coating method. The flakes agglomerates and formed a flower platelet. The agglomeration was increased slightly with higher annealing temperature and the flakes shattered when the BiOI was annealed at 450°C. The measurement shows rapid decline to ~200 nm at a temperature range of 450-550°C, which was due to loss of material through sublimation. This study provided significant output and a pathway for non-toxic BiOI thin film for perovskite solar cells.

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