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Study of Synthesis and Characterization of Bismuth Oxyiodide Thin Film for Non-Toxic Perovskite Solar Cells (Kajian Tentang Sintesis dan Pencirian Bismuth Oxyiodide Filem Nipis Untuk Perovskite Solar Sel Yang Tidak Beracun)

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ABSTRACT

Perovskite solar cells based on lead halide has demonstrated the fast increase in efficiency and advanced in photovoltaic technology in the last decade. However, perovskite solar cells that contain lead (Pb) has high efficiency but tangible risk to humans, animals, and the environment. Bismuth oxyiodide (BiOI) has been recognized as a suitable candidate of non-toxic material to replace lead without adversely impacting performance in perovskite solar cells. The interest in application of BiOI thin films is because BiOI has narrow band gap, high efficiency light absorption and high photo catalytic activity makes it the perfect contender to replace Pb as new non-toxic material perovskite solar cell. Thin films of BiOI were synthesized and deposited using Successive Ionic Layer Adsorption and Reaction (SILAR) on glass substrates. The same mole ratios of bismuth(III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) and potassium iodide (KI) were diluted in deionized water to achieve clear solution. The microscope glass was dipped consecutively in 0.01M of $(\text{BiNO}_3)_2 \cdot 5\text{H}_2\text{O}$ diluted in deionized water, 0.01M of (KI) diluted deionized water and 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 250 °C, 350 °C, 450 °C, and 550 °C for 20 minutes. The optical properties and structural properties of BiOI thin films were characterized using X-ray powder diffraction (XRD), Ultraviolet-visible (UV-Vis) measurement and Field Emission Scanning Electron Microscope (FESEM). The Surface Profilometer (SP) was used to measure the thin films thickness. The structure of the films changed with the annealing temperature. The color of the film changes to the orange-yellow and become more yellowish with increasing annealing temperature. The morphology of FESEM images demonstrated that the BiOI thin films have flakes morphology structure with the size around 1 μm . The deposited film thickness ranged between 3.479 μm and 8.082 μm . This study provided significant output and a pathway for non-toxic BiOI thin film for perovskite solar cells.

Keywords: Bismuth oxyiodide; dip coating; SILAR; thin film; perovskite solar cell

ABSTRAK

Perovskite solar sel berdasarkan plumbum halide diperlihatkan sebagai satu solar sel yang terpanas dan mempunyai kecekapan dalam fotovoltai teknologi dalam masa sedekad ini. Namun, perovskite solar sel dengan kecekapan yang tinggi mempunyai plumbum dan risiko yang ketara kepada manusia, haiwan, dan persekitaran. Bismuth oxyiodide (BiOI) adalah bahan yang tidak mempunyai plumbum, telah dikenali sebagai pengganti yang amat sesuai untuk menggantikan plumbum solar sel tanpa memberi impak dalam prestasi untuk perovskite solar sel. BiOI filem nipis mempunyai band gap yang sempit, kecekapan yang tinggi dalam daya penyerapan cahaya, dan tinggi dalam aktiviti photo catalytic menjadikan filem nipis BiOI paling sesuai untuk menggantikan plumbum sebagai bahan baharu untuk

solar sel tanpa menggunakan bahan plumbum. Film tipis BiOI telah disintesis menggunakan teknik *Successive Ionic Layer Adsorption and Reaction (SILAR)* diatas kaca substrat. Menggunakan nisbah yang sama untuk bismuth(III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) dan potassium iodide (KI) dicairkan tanpa sebarang haba sehingga menjadi jernih. Kaca mikroskop di celup berturut-turut di dalam 0.01M ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) yang telah dicampurkan di dalam air deionisasi, 0.01M (KI) yang telah dicampurkan di dalam air deionisasi dan dalam 50ml air deionisasi. Proses ini dilakukan sebanyak 30 kali celupan didalam ketiga-tiga bekas dan akhirnya sampel dikeringkan menggunakan udara suhu bilik. Kesemua sampel di penyepuhlandapan kepada beberapa suhu iaitu 250 °C, 350 °C, 450 °C, and 550 °C untuk 20 minit. Untuk sifat optic dan sifat struktur film tipis BiOI, dicirikan menggunakan *X-ray powder diffraction (XRD)*, *Ultraviolet-visible (UV-Vis) measurement* dan *Field Emission Scanning Electron Microscope (FESEM)*. Ketebalan film tipis dilakukan menggunakan *Surface Profiler (SP)*. Struktur untuk BiOI film tipis berubah mengikut kepada perubahan suhu penyepuhlandapan. Warna film tipis berubah daripada jingga kepada kuning dan menjadi lebih kekuningan dengan pertambahan suhu penyepuhlandapan. Untuk imej FESEM morfologi, ia menunjukkan BiOI mempunyai morfologi berbentuk serpihan struktur yang bersaiz dalam lingkungan 1 μm . Ketebalan film tipis pula, antara nilai 3.479 μm sehingga 8.082 μm . Kajian ini mempunyai kesan yang amat ketara dalam menggantikan BiOI sebagai bahan yang tidak bertoksik untuk aplikasi solar sel.

Kata kunci : Bismuth oxyiodide; lapisan celup; SILAR; film tipis; perovskite solar sel

INTRODUCTION

Perovskite solar cells (PSCs) hold advantage compared to other solar cells due to their speedy increment in conversion efficiency, simplicity, and low cost processing (Correa-Baena et al. 2017; Kim et al. 2019). All current PSCs with high efficiency containing harmful lead (Pb), which raises a serious environmental concern for large-scale growth. Not only is the danger to humans and living beings of lead contained in material wills, but it is also dangerous to the environment (Babayigit et al. 2016). In human, lead is harmful to the nervous and reproductive system. Therefore, in the perovskite structure, several researchers have tried to find another way to substitute Pb.

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 (Miller & Bernechea 2018; Frass et al. 2020; Kephart et al. 2016). The Pb-free material that is easy to synthesis is a bismuth-based compound with lower toxicity compared to others semiconductor materials and high tolerance in defect (Hahn et al. 2012). The most challenging part in thin film deposition and solar cell fabrication are to control the chemical composition of the material layers, homogeneity of film, thickness, lattice mismatch, cracks and pinholes formation, and existence of defect surface level (Hahn et al. 2012; Han et al. 2018; Wang et al. 2021).

Since Pb has the ns² valence electron, it can be replaced in the periodic table with bismuth (Bi), which sits

next to Pb. Bi can also be classified as a heavy metal, but compared to Pb, it has low toxicity. Based on this fact, Bi could offer a non-toxic material to replace Pb. It is known as a green element and has been widely used in cosmetic, personal care product, and medicines (Miller & Bernechea 2018). In addition, the promising material for photovoltaic materials can be considered another bismuth-based material, namely bismuth oxyiodide (BiOI), and this work will be studied. BiOI has narrower band gap energy which is around 1.59 eV with band edge absorption at 645 nm (Babayigit et al. 2016). BiOI is a semiconductor, which has attracted early interest. BiOI thin film can be deposited using chemical bath deposition (CBD), spin coating technique and Successive Ionic Layer Adsorption, and Reaction (SILAR) dip coating (Ezema 2005; Kariper, 2016; Putri et al. 2020; Putri et al. 2018). SILAR and CBD are highlighted among all the common methods in BiOI preparation for the application of solar cells. SILAR will be used for this study because it is simple and easy, low-cost, stable, and able to produce a uniform layer.

Since the analysis of the effect of annealing temperature on the preparation of BIOI thin film by SILAR is not yet published. The purpose of this paper is to examine and determine the structural, optical, and morphological properties by using successive ionic layer adsorption and reaction (SILAR). BiOI thin film will be synthesized and grown using SILAR technique under condition parameter that is annealing temperature. BiOI thin film will be annealed at various temperature to study the optical characterization, morphological structure, structural characterization, and electrical properties for each of the temperature.

EXPERIMENTAL METHOD

BiOI thin films have been deposited on glass substrate by using successive ionic layer adsorption and reaction (SILAR). The substrate used was commercial microscope glass slides ($26 \text{ mm} \times 76 \text{ mm} \times 1 \text{ mm}$). The glass slides were then cut to $20 \text{ mm} \times 30 \text{ mm}$ before dip coating process. Each of the substrate was cleaned with detergent and ethanol, and was sonicated in diluted ethanol for one hour, soaked in diluted hydrochloric acid, washed with deionized water, and then glass was drip dried in air (Ezema, 2005; Putri et al. 2018). The same mole ratios of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, and KI were dissolved in 50 ml deionized water for 30 minutes continuous stirring. The SILAR techniques are shown on Figure 1 where the dip time for each of the bath is 20 s. The glass dip was kept inclined in the beaker; based on how BiOI is easy to be deposited massively. This process has been repeated for 30 times and finally the sample was dripped and dried in air for 24 hours (Putri et al. 2018).

The physical appearance and morphological of BiOI thin film has been studied through the naked eye and FESEM. The thin film crystalline structural characterization optical will be characterized through X-ray diffractometer (XRD) and UV-Vis spectrophotometry. The film thickness of the films were measured with surface profilometer.

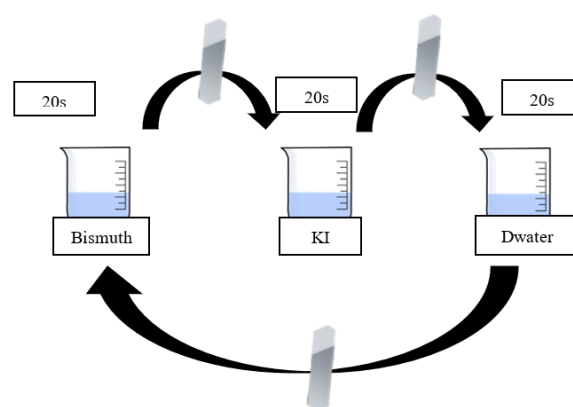


FIGURE 1. SILAR technique for dip coat

RESULT AND DISCUSSION

PHYSICAL OBSERVATION

From the physical observation through the naked eye, the deposited BiOI thin film shows a uniform layer with dark orange color. After the annealing process, the color of the film changes to the orange-yellow. Figure 2 shows the changes of color for film after annealing process for the annealing temperature of $250 \text{ }^\circ\text{C}$, $350 \text{ }^\circ\text{C}$, $450 \text{ }^\circ\text{C}$, and $550 \text{ }^\circ\text{C}$. The film becomes more yellowish with increasing annealing temperature. At $550 \text{ }^\circ\text{C}$, the color of the film changed to pale yellow.

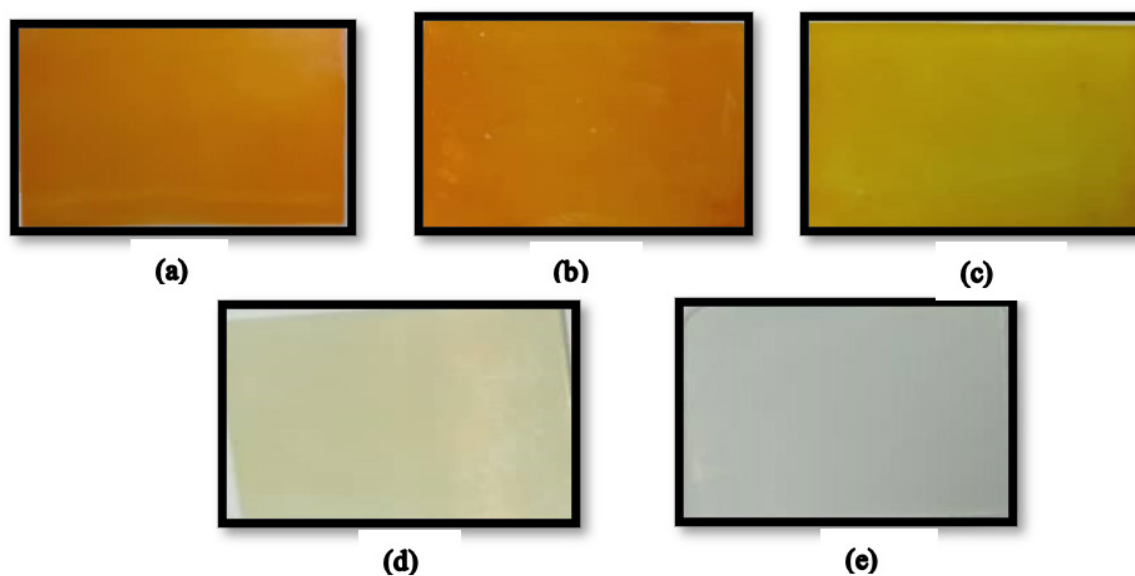


FIGURE 2. Physical observation for annealing temperature of (a) as deposited, (b) $250 \text{ }^\circ\text{C}$, (c) $350 \text{ }^\circ\text{C}$, (d) $450 \text{ }^\circ\text{C}$ and (e) $550 \text{ }^\circ\text{C}$

FIELD EMISSION SCANNING ELECTRON MICROSCOPY (FESEM) ANALYSIS

Field Emission scanning electron microscopy (FESEM) was used to examine the effects of change in the annealing temperature of the film surface morphology. The electric and optical properties of the film are directly affected by the surface properties. FESEM thin film images produced at different annealing temperatures are shown in the Figure 3. FESEM images (mag = 10k, WD = 8.4 mm and EHT = 5 kV) show different structures were formed and demonstrated that the BiOI thin films have flakes

morphology structure with the size around 1 μm . Here, the sheet-like material obtained may be influenced by the events during the synthesis process. The acidity of the solution, which has an effect on the various facets of BiOI can affect BiOI growth of the thin films. The flakes agglomerates and formed a flower platelet. The agglomeration was increased slightly with higher annealing temperature and the flakes were shattered when the BiOI was annealed at 550 $^{\circ}\text{C}$. Figure 4 shows FESEM images (mag = 20k, WD = 8.5 mm and EHT = 5 kV) in higher magnification for the thin films.

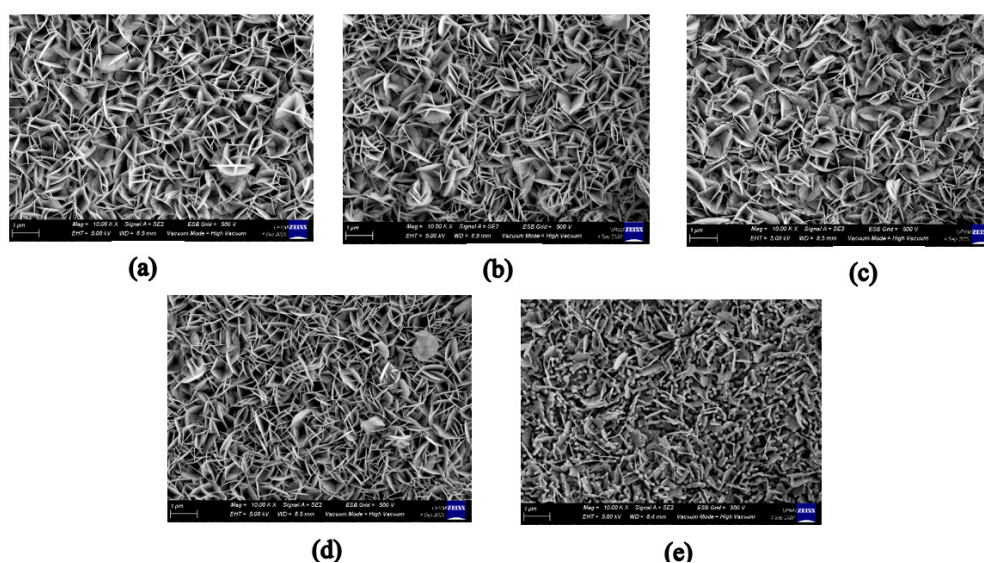


FIGURE 3. FESEM images (mag = 10k, WD = 8.4 mm and EHT = 5 kV) image of BiOI thin film with varied annealing temperature of (a) as deposited, (b) 250 $^{\circ}\text{C}$, (c) 350 $^{\circ}\text{C}$, (d) 450 $^{\circ}\text{C}$ and (e) 550 $^{\circ}\text{C}$

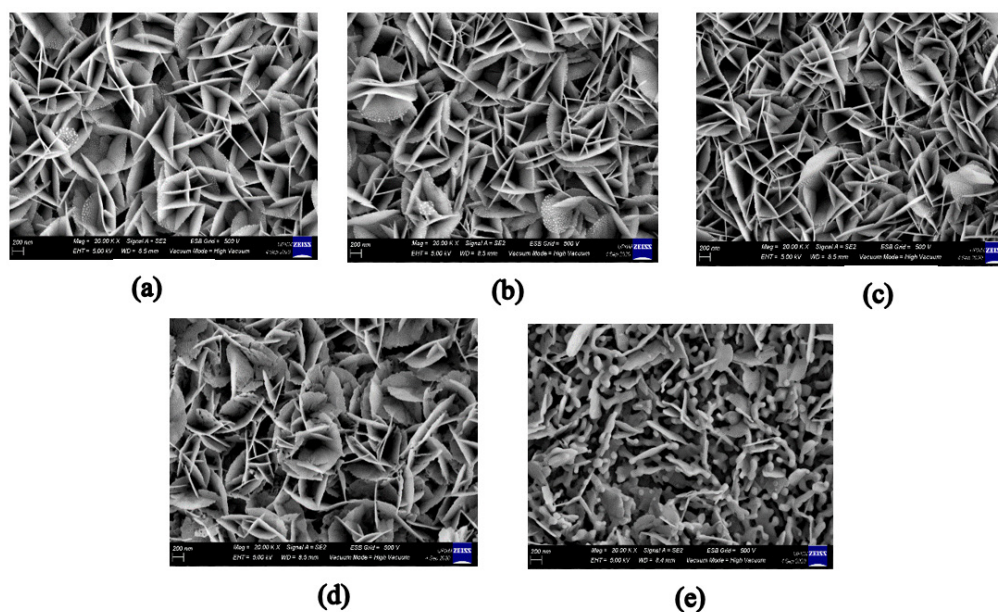


FIGURE 4. FESEM images (mag = 20k, WD = 8.4 mm and EHT = 5 kV) image of BiOI thin film with varied annealing temperature of (a) as deposited, (b) 250 $^{\circ}\text{C}$, (c) 350 $^{\circ}\text{C}$, (d) 450 $^{\circ}\text{C}$ and (e) 550 $^{\circ}\text{C}$

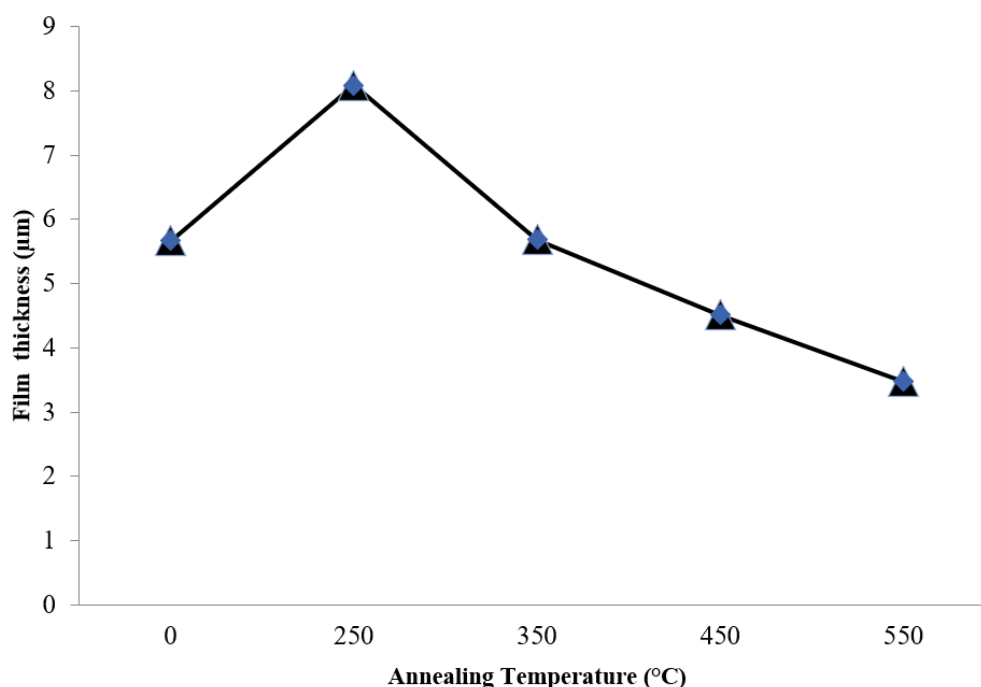


FIGURE 5. Thickness of the BiOI thin films

THICKNESS MEASUREMENT

The thickness of BiOI films is shown in Figure 5. By using a surface profilometer to measure the thickness of the film. Naturally, the thickness of the film indicates the difference in thickness when we anneal at various temperature. The highest film thickness was measured as 8.802 µm with annealing temperature of 250 °C. For the lowest film thickness recorded was for annealing temperature of 550 °C with 3.479 µm. Putri et al. (2020) produced BiOI with same deposition method and the thickness of the film was ranged 1-3 µm. Ezema (2005) produced BiOI by using chemical bath deposition (CBD) and thickness ranged 0.115-0.140 µm. Our films were thicker as compared with other researchers. This is due to the thickness of the film depending on the number of cycles during the SILAR process.

CONCLUSION

Thin films of bismuth oxyiodide (BiOI) were successfully deposited using successive ionic layer adsorption and reaction (SILAR) used in previous study. In this study, it shows that if we can control the dipping time and the concentration of the bath, surely the uniform layer of BiOI thin film will be easily deposited. Based on the result, it can be concluded that the annealing temperature for the

films can affect the film's optical and structural characterization. We can conclude that these BiOI thin films deposited using SILAR is also suitable for solar cell devices that we plan to fabricate on glass FTO and can promise good results for the solar cell devices.

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DECLARATION OF COMPETING INTEREST

None

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