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THE EFFECTS OF ANNEALING ON MICROSTRUCTURE, OPTICAL AND STRUCTURAL PROPERTIES OF BISMUTH OXYIODIDE THIN FILMS

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ABSTRACT

Perovskite solar cells based on lead (Pb) halide has demonstrated the rapid increase in efficiency and advanced in photovoltaic technology during this last decade, but the toxicity issue impede the large-scale industrial production. Bismuth oxyiodide (BiOI) has been recognized as suitable candidate of less-toxic material to replace Pb in conventional Pb-halide perovskite solar cells (PSCs), without adversely impacting performance in perovskite solar cells. Thin films of BiOI were synthesized and deposited using Successive Ionic Layer Adsorption and Reaction (SILAR) on glass substrates. The same molar ratios of bismuth (III) nitrate pentahydrate (Bi(NO3)5H2O) and potassium iodide (KI) were used in this experiment. The samples were annealed at various annealing temperature from 250 °C, 350 °C, 450 °C and 550 °C, for 20 minutes. The physical observation, microstructure, average thickness, optical and structural properties of BiOI thin films were characterized using macroscopic examination, field-emission scanning electron microscope (FESEM), surface profilometer (SP), ultraviolet-visible (UV-Vis) and X-ray diffraction (XRD), respectively. From the physical observation, the colour of the films changed from the orange yellow to yellowish with increasing annealing temperature. The microstructure study demonstrated the BiOI thin films have flakes morphology structure. The average thicknesses of BiOI films were in ranged of 3.479 - 8.082 µm with the optical band gap, for example in range 1.607 to 2.150 eV. From XRD characterization, sample annealed below 350 °C demonstrated single crystalline structure, but at higher annealing, BiOI film changed to polycrystalline with mixed phases of BiO. The crystallite size was calculated in range from 27.747 to 29.314 nm. This study provided some clue on BiOI thin film properties for active layer in low-toxicity perovskite solar cells.

1.0 INTRODUCTION

In photovoltaic solar cell devices, a material absorber, formerly known as an active layer, is responsible for harvesting light to carry the charge carrier. Perovskite solar cells (PSCs) have an advantage over other solar cells due to their quick increment in conversion efficiency, simplicity and low-cost processing [1-2]. However, the existing PSCs that exhibit high efficiency contain harmful lead (Pb). In lead perovskite solar cells, lead remains problematic to the environment which raised severe environmental concerns for large-scale production, it poses risks to human and other living things when the lead is contained in material wills and is detrimental to the environment [3-4]. In addition, it has another issue, where Pb-perovskite has instability in its application. Pb-perovskites are easily decomposed with the metyl ammonium Pb-iodide (MAPI) structure because of humidity, UV light and high temperatures [5-6]. Therefore, researchers tried to find an alternative way to substitute Pb with other materials in the perovskite solar cells active layer.

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Since Pb has the ns^2 valence electron, it can be replaced in the periodic table with Bismuth (Bi), which sits next to Pb. Bismuth oxyiodide (BiOI) has been recognized as the electronic structure necessary to replicate Pb-halide perovskite. Bi can also be classified as heavy metal, but it has lower toxicity compared to Pb. It is a green element and has been widely used in cosmetics, personal care products, and medicines [7]. BiOI has a narrow band gap around 1.6 eV with band-edge absorption at 645 nm, efficient light absorber and high Shockley-Queisser limit [4, 7-8]. Moreover, bismuth-based compound has high tolerance in defect and is feasible to be synthesised compared to others semiconductor materials [8–12]. BiOI thin film can be grown using chemical bath deposition (CBD) [13, 14], spin coating technique [15] and Successive Ionic Layer Adsorption and Reaction (SILAR) dip coating [16]. Nevertheless, the most challenging part in thin film deposition and solar cell fabrication is the step of controlling the chemical composition of the material layers, homogeneity of film, thickness, lattice mismatch, cracks, pinholes formation and defect surface level [11-12].

The effect of annealing temperature on BiOI thin film prepared by the SILAR method is yet to be reported elsewhere. Therefore, this work systematically explores the effect of annealing temperature on BiOI thin film synthesized and grown using the SILAR technique. The microstructures, thickness measurement, optical studies and structural properties of the BiOI films were characterized using FESEM, surface profiler, UV-Vis spectrophotometry and X-ray diffraction (XRD) respectively.

2.0 EXPERIMENTAL METHOD

BiOI thin films have been deposited on glass substrate by using the SILAR technique. The substrate used in this study is a commercial microscope glass slide with 26 mm × 76 mm × 1 mm. The glass slides were cut to the area size of 20 mm × 30 mm before the cleaning process. Each substrate was cleaned with detergent and ethanol at the first step followed by sonication in diluted ethanol for 1 hour and soaked in diluted hydrochloric acid. The substrates were next rinsed with deionized water and dried in the air.

To prepare the synthesized solution, two solution baths were prepared. The first bath was 0.5 M of bismuth (III) nitrate ($Bi(NO_3)$) diluted in 50 ml deionized water while the second bath was 0.5 M potassium iodide (KI) diluted in 50 ml deionized water. Both solutions were continuously stirred for 30 minutes. The set-up of the SILAR deposition method is shown on Figure 1. One beaker containing deionized water was prepared as the rinse bath of each cycle. The dipping time of the glass substrate into each chemical was 20 seconds. During the dipping process, the substrate was positioned inclined in the beaker. The dipping cycle process was repeated 30 times to obtain a thicker layer suitable for the solar cells followed by dripping the substrate in air.

The deposited BiOI thin films were annealed at four different temperatures at 250 °C, 350 °C, 450 °C and 550 °C for 20 minutes. One as-deposited BiOI thin film was kept as a reference sample in this study. The physical appearance of BiOI thin film has been observed physically. The microstructures of the films were characterized using the FESEM model Geminis SEM 500. The thickness measurement, optical studies and structural properties of BiOI thin films have been characterized using optical profiler model The Dektak® 150, UV-Vis spectrophotometry model Lambda 750 (Perkin Elmer) and X-ray diffraction (XRD) model D8 Advance (Bruker AXS), respectively.

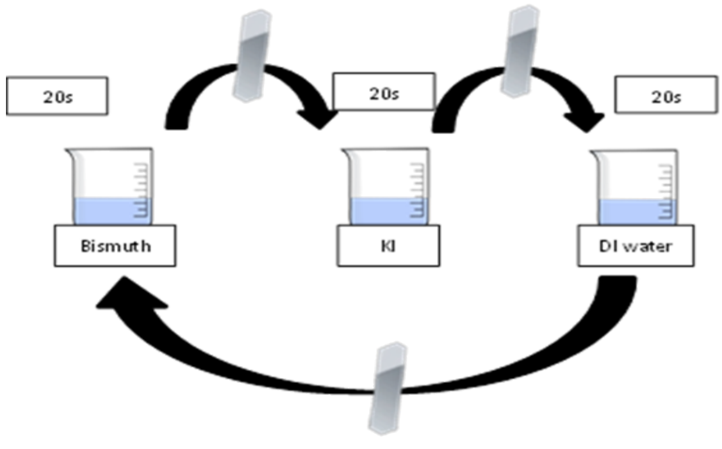

Figure 1. SILAR technique for dip coating

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3.0 RESULTS AND DISCUSSIONS

3.1 Physical Observation

Figure 2 shows the physical appearance and colour of the deposited BiOI thin films for (a) as-deposited film and films annealed at (b) 250, (c) 350 (d) 450 and (e) 550 °C. The as-deposited BiOI thin film showed a uniform layer with dark orange colour. After the annealing process at 250 °C, the colour of the film has changed to orange-yellow, and the film becomes more yellowish with increasing annealing temperature. At the highest annealing temperature 550 °C, the colour of the film changed to pale yellow.

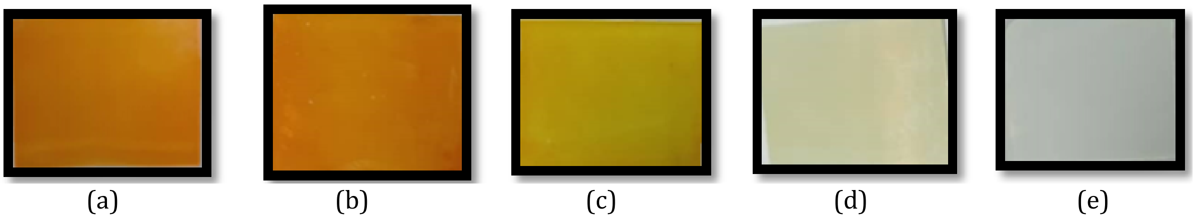

Figure 2. Physical observations for annealing temperature of (a) as deposited, (b) 250 °C, (c) 350 °C, (d) 450 °C and (e) 550 °C

3.2 Field Emission Scanning Electron Microscopy (FESEM) Characterization

Field emission scanning electron microscopy (FESEM) was used to study the effects of BiOI thin film microstructure annealed with various temperatures. The images toleration was taken at 20 k magnification, 8.4 mm working distance and 5 kV electron high tension (EHT). Figure 3 shows that the BiOI thin films had flakes morphology structure with the thickness of flakes size viewed from the top images around 0.02 μm. The sheet-like material obtained might be influenced by the events during the synthesis process. The acidity of the solution, which effects on the various facets of BiOI, can affect the BiOI growth of the thin films. The FESEM images showed that, the BiOI film morphology formed flakes agglomeration such as flower platelet after being annealed at 450 °C. However, the agglomeration and the flakes were shattered when the BiOI was annealed at 550 °C. This observation could be due to the too high annealing temperature heat treatment that has started deteriorating the BiOI layer. Figure 3(f) shows the cross-section of BiOI thin film for as-deposited BiOI. It is proven that the layer form with a flake shape structure from the side view of the layer. Flakes shape morphology is suitable for solar cell devices since there is no grain boundary throughout the layer, which could produce good electron mobility in the solar cell devices.

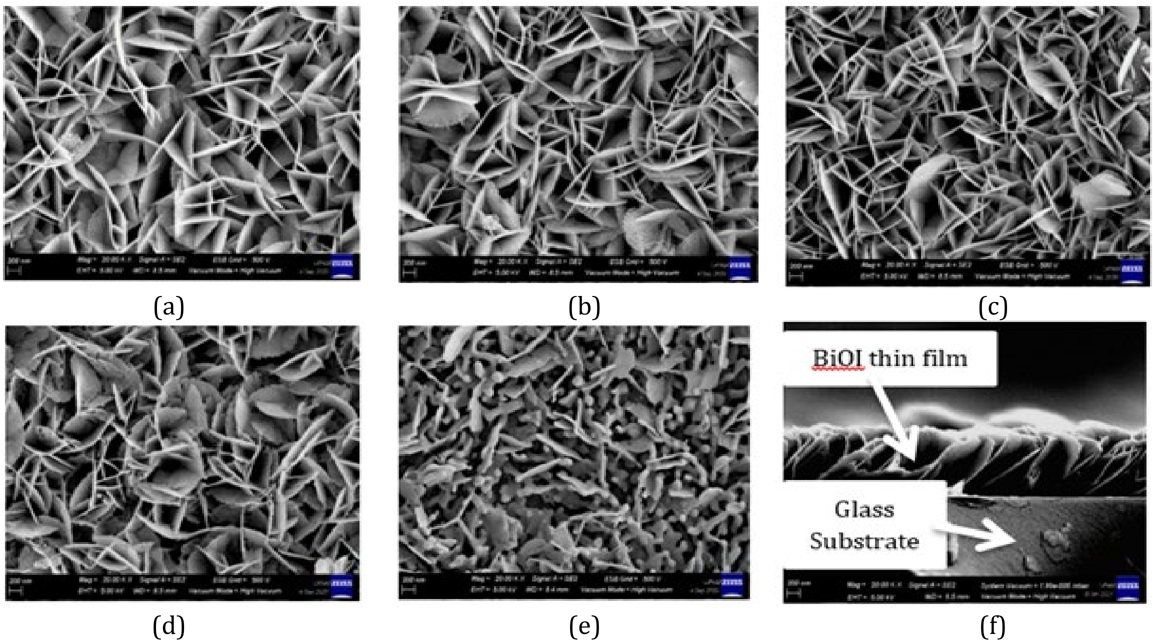

Figure 3. FESEM image of (a) as-deposited BiOI thin film and annealed BiOI films at, (b) 250 °C, (c) 350 °C, (d) 450 °C and (e) 550 °C. Figure (f) shows the cross-section image of as-deposited BiOI thin film

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3.3 Thickness Measurement

A surface profilometer was used to measure the thickness of the film and the thicknesses of BiOI thin film for as-deposited layer and annealed at temperature of 250 °C, 350 °C, 450 °C and 550 °C are shown in Figure 4. It is observed that the highest film thickness was 8.802 µm for the sample with an annealing temperature of 250 °C and the lowest film thickness recorded was for BiOI layer annealing at a temperature of 550 °C with 3.479 µm. Based on this measurement, it suggested that high annealing temperature is not helpful in this study since it could cause material sublimation.

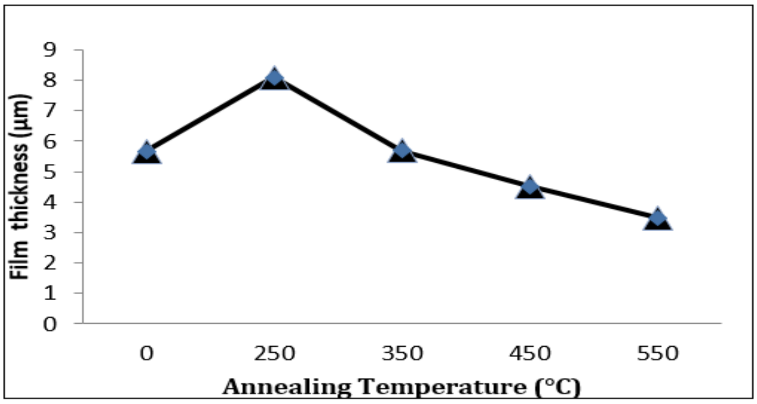

Figure 4. Thickness of the BiOI thin films

3.4 Optical Properties Of BiOI Thin Films

The UV-Visible spectra are displayed in Figure 5. From the physical observation, the BiOI thin film annealed at too high temperature showed higher transparency than others. The energy band gap was estimated by extrapolating the straight-line segment of the graph to the photon energy axis as shown in Figure 5. Figure 5 shows the optical absorption of the as-deposited BiOI thin film and annealed layer at 250 °C, 350 °C, 450 °C and 550 °C respectively. The average error of these measurements was ± 0.02 eV. The trend and value of the band gap are shown in Figure 6 and Table 1.

From Figure 6, it is shown that the BiOI layer annealed at 350 °C shows the lowest E_g value with 1.61 eV. The decrease in the energy bandgap for BiOI film at annealing temperature 350 °C can be due to the re-crystallisation, increase in grain size and lower defects [20]. On the other hand, the highest E_g value was obtained for the sample annealed at 550 °C with 2.15 eV. This result shows that BiOI film annealed with temperature of 350 °C demonstrated the optimum characteristic with the lowest bandgap that suits for absorbance layer in perovskite solar cells. Lower energy band gap is sought after in photovoltaic materials since it is easier for valence electron in the valence band to jump into the conduction band in order to conduct current.

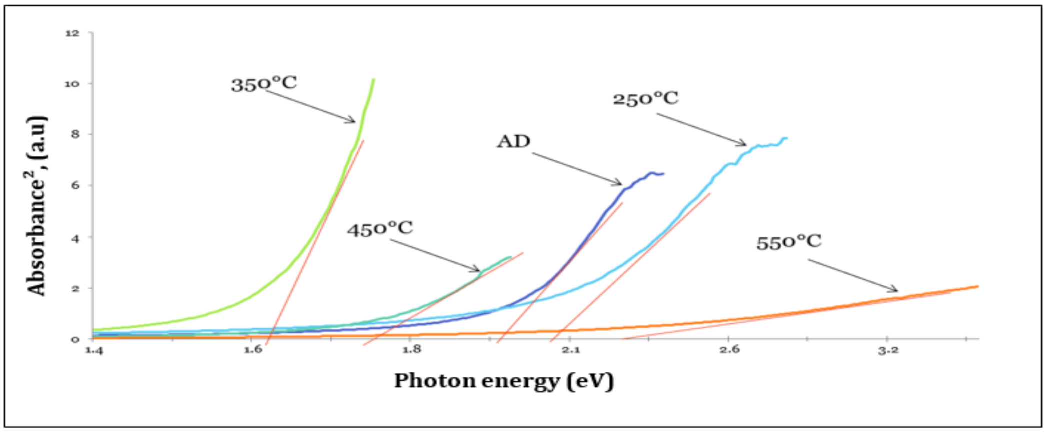

Figure 5. Absorbance^2 vs photon energy of as deposited, 250 °C, 350 °C, 450 °C and 550°C

Table 1. Energy band gap for BiOI thin films

Annealing Temperature, (°C)	Energy Band Gap, E_g (eV) (± 0.02 eV)
As deposited	1.98
250	2.08
350	1.61
450	1.75
550	2.15

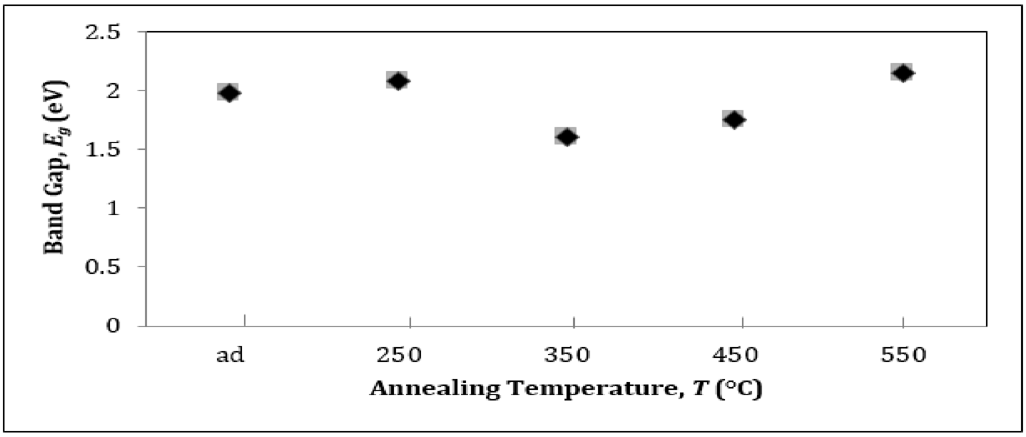

Figure 6. Variation of Energy band gap E_g of as-deposited BiOI layer and film annealed at 250 °C, 350 °C, 450 °C and 550 °C

3.5 Structural Characterization of BiOI Thin Films

X-ray diffraction (XRD) is a technique used to investigate the crystalline phases present in BiOI thin films and measure the structural properties including the phase composition and preferred orientation. The XRD patterns of the as deposited and annealed BiOI layers are shown in Figure 7. The XRD of a glass substrate was inserted as a reference. An intense peak tetragonal BiOI thin film was observed at 2θ = 29.28, 31.68, 45.04, and 54.68°. These peaks are assigned to the crystal plane of (102), (110), (200), and (105), respectively. The appearance of these peaks has been reported in tetragonal phase pattern for BiOI thin film from the previous research [15, 17]. There was no impurity found in the samples. Typically, BiOI compounds own a tetragonal structure [18]. Based on Figure 7, the results showed that all peaks matched those of tetragonal BiOI (P4/nmm, space group 129) [18-19] for as-deposited BiOI and annealed at 250 °C and 350 °C. This observation is due to the nature preferred growth direction of BiOI. A similar pattern of as-deposited BiOI and annealed at 250 °C and 350 °C with no mixture of other material were also observed.

However, BiOI annealed at 450 °C and 550 °C showed different patterns. Due to these results, a combination of BiOI and $Bi_5O_7I_3$ materials have been found. According to the BiOI sample annealed at 450 °C, it became single crystalline with a dominant peak at 2θ = 28.12°. However, for the sample annealed at 550 °C, the appearance of new crystalline peaks was observed as small peaks at 2θ = 29.15° and 35.35° which belongs to $Bi_5O_7I_3$ material with orthorhombic phase. This observation indicated that BiOI films annealed at 450 °C and 550 °C are polycrystalline with mixed phases. The too-high annealing temperature induces the phase transition from a single tetragonal phase to the mixture of orthorhombic and tetragonal phases [24]. This work shows that BiOI thin film annealed at 350 °C showed the highest crystalinity. Therefore, it suggested that the film has the highest order of atomic arrangement, which is homogenous and more stoichiometric. The crystal size, D was calculated using the Debye-Scherrer equation in (1):

$$D = \frac{K\lambda}{\beta Cos\ \theta} \quad (1)$$

where K is constant (0.9), λ is Cu wavelength (0.154 nm), β is the full width at half maximum (FWHM) in radian, and θ is the Bragg angle for the diffraction peaks. From Table 2, the optimum peak of (110) BiOI showed a slight increase in crystallite sizes and was highlighted in the table. Therefore, it is noticeable

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that the heating process had an impact on crystal size distribution. Based on XRD measurements, it is suggested that a suitable annealing temperature and time is at 350 °C.

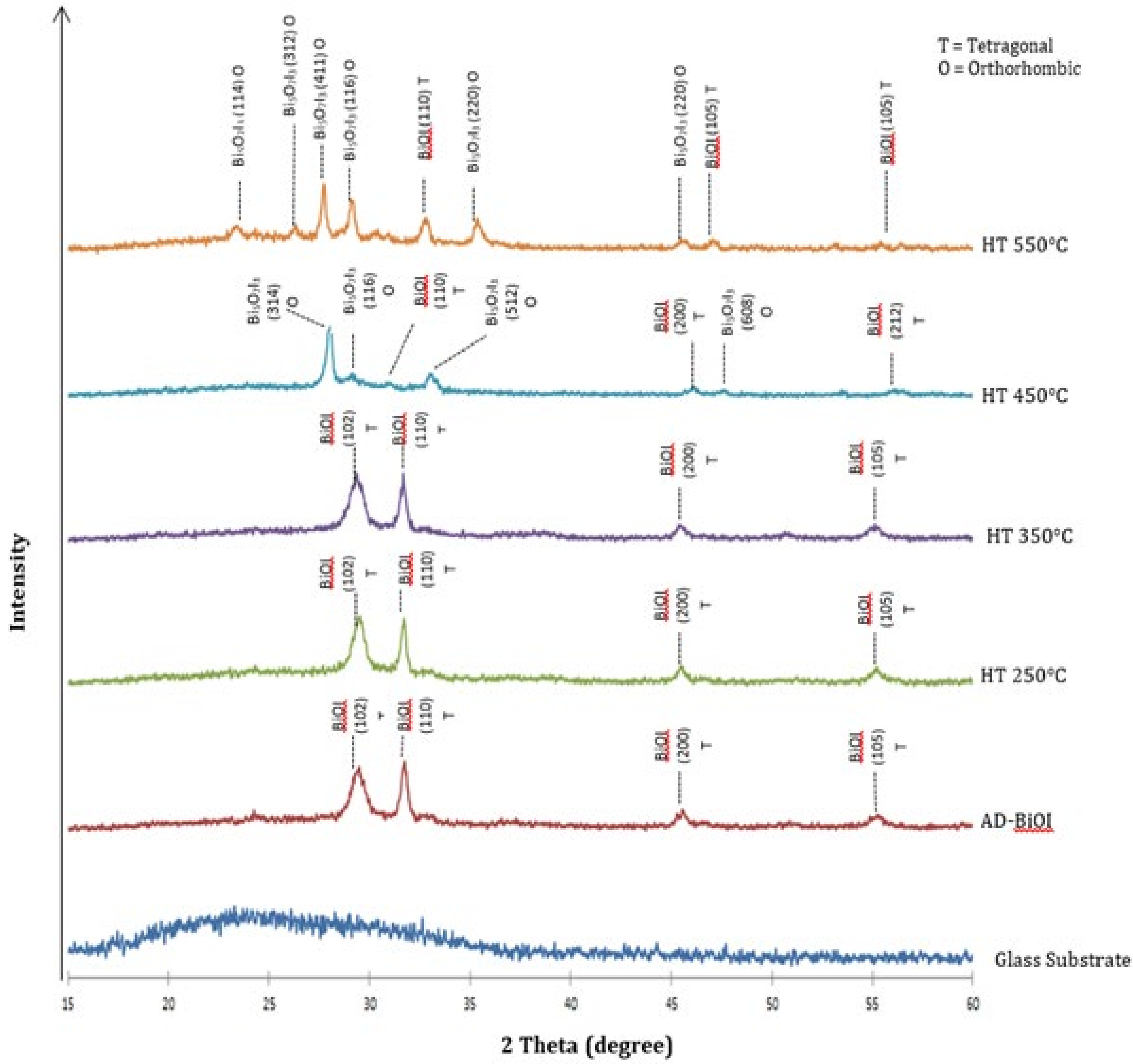

Figure 7. XRD patterns of glass substrate and BiOI thin films as deposited BiOI and film annealed at 250 °C, 350 °C, 450 °C and 550°C

Table 2. Summary of XRD data for BiOI thin films

Sample (°C)	Angle (2θ)	Intensity Relative to the peak at ~29° (%)	FWHM (Degree)	Crystallite size, D (nm)	Plane of Orientation (h k l)	Assignment	
(AD)	29.280	92.05	0.296	27.747	(1 0 2)	Tetragonal	BiOI
	31.990	100	0.318	26.019	(1 1 0)	Tetragonal	BiOI
	45.520	33.42	0.455	18.927	(2 0 0)	Tetragonal	BiOI
	55.200	26.30	0.552	16.228	(1 0 5)	Tetragonal	BiOI
(250)	29.400	100	0.296	27.783	(1 0 2)	Tetragonal	BiOI
	31.720	96.78	0.317	26.006	(1 1 0)	Tetragonal	BiOI
	45.520	31.57	0.455	18.927	(2 0 0)	Tetragonal	BiOI
	55.160	29.82	0.553	16.190	(1 0 5)	Tetragonal	BiOI
(350)	29.280	100	0.295	27.823	(1 0 2)	Tetragonal	BiOI
	31.680	99.48	0.317	26.040	(1 1 0)	Tetragonal	BiOI
	45.360	27.72	0.556	15.480	(2 0 0)	Tetragonal	BiOI
	55.120	29.02	0.552	16.242	(1 0 5)	Tetragonal	BiOI
(450)	28.119	100	0.281	29.133	(3 1 4)	Orthorhombic	Bi5O7I3
	29.225	35.40	0.292	28.105	(1 1 6)	Orthorhombic	Bi5O7I3

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Sample (°C)	Angle (2θ)	Intensity Relative to the peak at ~29° (%)	FWHM (Degree)	Crystallite size, D (nm)	Plane of Orientation (h k l)	Assignment	
	30.953	22.57	0.310	26.581	(1 1 0)	Tetragonal	BiOI
	33.095	36.03	0.331	25.028	(5 1 2)	Orthorhombic	Bi5O7I3
	45.360	18.43	0.451	19.084	(2 0 0)	Tetragonal	BiOI
	46.100	13.04	0.463	18.640	(6 0 8)	Orthorhombic	Bi5O7I3
	56.322	14.91	0.562	16.025	(2 1 2)	Tetragonal	BiOI
	23.328	41.25	0.234	34.652	(1 1 4)	Orthorhombic	Bi5O7I3
	24.624	42.75	0.239	34.009	(3 1 2)	Orthorhombic	Bi5O7I3
	27.870	100	0.271	30.181	(4 1 1)	Orthorhombic	Bi5O7I3
	29.150	76.25	0.289	28.392	(1 1 6)	Orthorhombic	Bi5O7I3
(550)	32.692	54.00	0.325	25.464	(1 1 0)	Tetragonal	BiOI
	35.348	53.00	0.351	23.745	(2 2 0)	Orthorhombic	Bi5O7I3
	45.472	21.00	0.452	19.049	(5 2 3)	Orthorhombic	Bi5O7I3
	46.974	23.25	0.459	18.864	(2 0 0)	Tetragonal	BiOI
	56.454	19.25	0.565	15.952	(1 0 5)	Tetragonal	BiOI

4.0 CONCLUSION

BiOI thin films were successfully grown via the SILAR technique. BiOI layers demonstrated good adhesion to the glass substrate. The annealing temperature for BiOI thin films has been studied at 250 °C, 350 °C, 450 °C, and 550 °C, respectively. The physical observation and thickness measurement showed that the high annealing temperature could cause material sublimation and deterioration. The morphology study from FESEM showed an improvement of flakes size with higher annealing temperature. However, cracks and deterioration formed when the layer was annealed at 450 °C and above. The band gap energy was in the range of 1.607 to 2.150 eV. The crystallite size of the optimum peak in XRD increased with annealing temperature and was associated with the FESEM result. However, the too high annealing converted the single crystalline BiOI film into polycrystalline structure. Based on this study, the optimum properties of BiOI thin film as active layer for perovskite solar cells were observed for the sample annealed at 350 °C with E_g of 1.61 eV.

5.0 ACKNOWLEDGEMENT

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