The effects of micro and macro structure on electronic properties of bismuth oxyiodide thin films

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Abstract

Bismuth oxyiodide (BiOI) thin film was deposited using successive ionic layer adsorption and reaction (SILAR) technique under the same molar ratio of bismuth (III) nitrate pentahydrate (Bi(NO₃)₅H₂O) and potassium iodide (KI). The effects of micro and macro structures due to the post-annealing treatment has been studied towards the improved electronic properties of BiOI films. BiOI thin film was perfectly coated without any cracks or pinholes. The as-deposited BiOI film displayed small flakes with flower shape microstructure. The flakes size has increased from ~0.8 μm to ~3.2 μm upon annealing at 350 °C, thenceforth shattered with increasing annealing temperature. BiOI films annealed at 350 °C showed a sharper band edge slope with an energy bandgap ~1.61 eV compared to others annealing temperatures. The single crystalline BiOI film has transformed from tetragonal to tetragonal-orthorhombic polycrystalline with mix Bi₅O₇I₃ and Bi₇O₉I₃ phases after being annealed >450 °C. Electronic properties of BiOI were studied in terms of average resistance and conductivity measured using four-probe hall effect measurement. The conductivity value has reached the maximum for sample annealed at 350 °C, owing to the formation of ordered phase in material structure, higher crystallinity, larger flakes sizes, as well as reduction of defects and grain boundaries resistance. When the annealing temperature exceeded 450 °C, the electrical conductivity decreased due to the particle aggregation, sublimation of materials, formation of mix-phase and polycrystalline structure that generated grain boundaries and provided more resistance for electrons flow. The work has demonstrated a better understanding of material issues and some clues on the effect of the thickness, microstructure and structural properties on the electronic properties of BiOI thin film.

Introduction

Due to the current demands for green perovskite solar cells (PSCs), lead-free materials have become a hotbed of research to meet current industrial needs [1–3]. Among the available lead-free halides that have been developed, bismuth oxyhalides (BiOX; X = Cl, Br, I, and F) have drawn great research interest due to their outstanding electrical and optical properties [4, 5]. Bannister et al have first reported the crystal structure of BiOX in 1935 [6]. The BiOX compounds belong to a group of V-VI-VII ternary oxide semiconductors with a tetragonal structure. The chemical expression of the group is commonly expressed as [M₂₋₂X₂][Xₘ]n, where M and X are metal and halide, respectively. Among the bismuth oxyhalides family such as BiOI, Bi₅O₇I₃, Bi₇O₉I₃, and Bi₁₀O₁₃I₉, bismuth oxyiodide (BiOI) has been reported as excellent electronic structure that necessary to replicate Pb-halide perovskite for lead-free PSCs, high tolerance in defect and smallest bandgap (Eg) of ~1.63–2.1 eV [7–10]. BiOI thin film can be deposited using chemical bath deposition (CBD) [11, 12], spray pyrolysis [13] and modified successive ionic layer adsorption and reaction (SILAR) [14, 15]. SILAR method will be used in this study because of the simplicity, the characteristics of being repeatable and ability to produce a uniform layer.
Although BiOI perovskites were discovered several decades ago, there are still questions regarding the relationship between the micro and macro structure and the electronic properties of these materials. Strategies such as post-deposition annealing treatment, controllable synthesis and modification of the materials have been used to enhance its properties [16–18]. Post-annealing treatment is a great practice in fabrication to alter the microstructure and structural of a material in order to change the mechanical or electrical properties. This method is essential to eliminate the inevitable defects and surface dangling bond during the film formation, thus improving crystal growth as well as reducing grain boundaries for better carrier movements in BiOI thin films [19–22].

Detailed reviews that highlight electronic behaviours in BiOI films are very important for new researchers and readers in the field of material chemistry, to provide better knowledge on the recent research progress in this field. Based on the literature review, there is no systematic analysis or reviews on the influence of film thickness, structural and microstructure on electronic properties of BiOI thin film. This paper presents an original investigation on the effect of micro and macro structure of BiOI film under various annealing temperatures on the electronic properties.

**Methodology**

To characterise the microstructural, structural and electrical properties of BiOI, a group of samples was prepared as thin films by employing the SILAR technique. Two solutions have been prepared prior to the deposition. The first solution, bismuth nitrate pentahydrate (Bi(NO$_3$)$_3$·5H$_2$O) was prepared by mixing 0.1 M of bismuth nitrate (Bi(NO$_3$)$_3$) and 0.001 M of nitric acid (HNO$_3$) for three hours at room temperature. Both (Bi(NO$_3$)$_3$) and HNO$_3$ had a purity of 99% in 100 ml deionised water. The second solution was prepared by diluting 0.1 M Potassium Iodide (KI) in 100 ml of deionised water. Standard microscope glass was used as substrate in BiOI film deposition for thickness, microstructural and structural characterisation while glass/FTO substrate was used to grow BiOI film for characterisation of electronic property.

The deposition procedure was started by immersing the substrate in an aqueous solution of (Bi(NO$_3$)$_3$·5H$_2$O) for 10 s, followed by immersing in KI solution for 20 s for chemical reaction. Immediately after the sample was removed from the solutions, it was dipped in deionised water, rinsed and dried to one complete cycle. The process was repeated for 30 cycles to obtain a uniform BiOI thin film. A study on the dipping cycle was done prior to this study. The best layer was decided in terms of the physical appearance and morphological homogeneity of the as-deposited sample and the ability of the layer to withstand rapid changes in temperature during annealing. The process of this technique is illustrated in figure 1.

Finally, the deposited BiOI thin films were then annealed at 250°, 350°, 450° and 550°C for 20 min. In this study, we used an as-deposited (AD) BiOI film as a reference sample. The thickness, optical, microstructural, structural and electronic properties of BiOI thin films have been studied through optical profilometry, UV–vis spectrophotometry, scanning electron microscope (SEM), X-ray diffraction (XRD) and four-probe hall effect measurement, respectively.

**Result and discussion**

(i. **Thickness, optical and microstructure effects in the electrical properties**)

BiOI thin films were successfully grown by SILAR techniques, and they demonstrated good adhesion to the glass substrate. The thickness of BiOI thin films was characterised using optical profilometry as shown in table 1. Based on the results, the average thickness of as-deposited BiOI film was ~5.66 μm, suggesting that the growth rate of the films by SILAR was about 188 nm cycle$^{-1}$. When annealed at 250°C, the thickness had increased to 8.08 μm, but it was further reduced to 7.98 μm at 350°C, indicating the micro and macro-structural features such as density, porosity and crystalline morphologies had been improved with appropriate annealing temperature. However, the thickness was decreased significantly to approximately 6.51 μm when the annealing temperature was increased to 450°C. It demonstrated a rapid decline to almost half of the original thickness (~3.48 μm) when the annealing temperature was increased to 550°C. The rapid reduction in the average thickness had increased the resistance in the films caused by shrinkage and densification of the thin films, which could happen due to particle aggregation and grain coalescence.

It is suggested that the annealing process could reduce the dislocation density and strain value, hence improving the crystallinity of the film. The advantage of the decrease in dislocation density is that it can increase the electrical conductivity of the films [23]. Likewise, materials will transform into a more ordered phase during annealing and reduce defect states in the forbidden band gap. However, appropriate annealing temperature should be considered in this study since extremely high annealing temperature could cause dimensional changes.
due to shrinkage, hence reducing the film thickness and material deterioration. The trend of average thickness as a function of annealing temperature is shown in Figure 2.

The optical absorption measurements of the BiOI layers were carried out using UV–vis spectrophotometry in the wavelength range of 400–900 nm. The square of absorbance ($A^2$) has been plotted as a function of photon energy, and the energy band gap, $E_g$ was estimated by extrapolating the straight-line segment of the graph to the photon energy axis. Figure 3 shows the optical absorption spectra of BiOI thin films annealed at temperatures ranging from 250° to 550 °C. It is observed that the energy bandgap of the as-deposited BiOI films was in the range of 1.61 to 2.15 eV. The bandgap of the BiOI layer increased slightly when annealed to 250 °C, but decreased to $\sim$1.61 eV when annealed at 350 °C. The observation could be due to the result of the crystallisation where there is an increase in flakes size and lower defects [18]. The close value of the bulk BiOI can be obtained if the atoms are better arranged in the crystal lattice. Also, the slope of the band edge is much sharper at 350 °C which suggests that there are fewer shallow donors and acceptors exist in these stoichiometric layers. The presence of defects or impurities in as-deposited BiOI disturbs the lattice and leads to low light absorbance. The appropriate annealing temperature helps the atom to form better crystalline lattices. BiOI annealed at temperatures of 450° and 550 °C showed a drastic increment of bandgap, which could be due to the sublimation of the material at the extremely high annealing temperature. The summary and trend of the optical energy bandgap with different annealing temperatures is shown in Table 1 and Figure 4.

The average resistance of the FTO/BioI/Au structure was measured using the four-probe hall effect measurement. The electrical conductivity was calculated with known thicknesses of the BiOI layer. Table 1

| Table 1. The summary of thickness and electrical properties of BioI thin films annealed at different temperatures. |
|---|---|---|---|---|---|
| Annealing temperature (°C) | Average thickness (±0.02 μm) | Average resistance $\times 10^4$ (Ω) | Energy band gap, $E_g$ (±0.5 eV) | Resistivity, $\rho \times 10^4$ (Ωcm) | Conductivity, $\sigma \times 10^{-3}$ (Sm⁻¹) |
| As-deposited | 5.66 | 90.80 | 1.98 | 8.02 | 1.25 |
| 250 | 8.08 | 52.80 | 2.08 | 3.03 | 3.33 |
| 350 | 7.98 | 10.30 | 1.61 | 0.66 | 15.24 |
| 450 | 6.51 | 0.03 | 1.75 | 2173 | 0.0046 |
| 550 | 3.48 | 0.09 | 2.15 | 13012 | 0.00077 |

Figure 1. The dipping process and annealing parameters of BiOI thin films.
Figure 2. Average thicknesses and average resistances of BiOI films for as-deposited and annealed at 250° to 550 °C.

Figure 3. Optical absorption of BiOI thin films for as-deposited and annealed at temperatures ranging from 250° to 550 °C.

Figure 4. The conductivity and band gap measurements of BiOI for as-deposited and at various annealing temperatures. The inserted figure is an SEM image of (a) as-deposited and annealed BiOI films at (b) 350 °C and (c) 550 °C.
shows the measurements of average resistance, resistivity and conductivity of BiOI thin films as a function of the annealing temperature. The graph of the conductivity and energy bandgap versus annealing temperatures is presented in figure 4. In addition, the SEM images for as-deposited BiOI thin films and after annealed at 350 °C and 550 °C were added in the inset of figure 4.

Based on the results, it is observed that the electrical conductivity of BiOI film decreased slightly at the annealing temperature of 250 °C when compared to the as-deposited layer. The conductivity increased from $1.25 \times 10^{-5}$ to $1.52 \times 10^{-4}$ Sm$^{-1}$ and achieved the highest peak after being annealed at 350 °C. The enhancement in the conductivity is due to the improvement of crystallinity, the enlargement of the flake size and the reduction of defects which promote the higher mobility of electrons [20, 21, 24]. As shown in figures 4(a) and 5(a), the as-deposited BiOI film consists of agglomerations of flakes with flower shapes. Due to the agglomerations, the electrons suffer grain boundary scattering when travelling in both directions, which are parallel and vertical to the substrate. Therefore, the measured conductivity is relatively low. During the annealing process, these agglomerations and smaller flakes increased from $\sim 0.8$ μm to $\sim 3.2$ μm after being annealed at 350 °C as shown by the SEM images in figure 5(c) and in the inset of figure 4(b). Thus, the electrons can move along the fully crystalline grains from the FTO to Au contacts, as there are no grain boundaries to hinder the charge carrier movements. The results demonstrated the benefits of having micro-size columnar type flakes in the solar cell. In addition to the high conductivity, the larger flakes microstructure introduces active photovoltaic (PV) junction along the grain boundaries due to melting and diffusion of doped into BiOI materials. The combination of these vertical junctions at the boundaries together with the main rectifying junction leads to the transfer of electrons and holes in different paths and minimise the recombination [25, 26]. This finding will provide the future research direction for producing high-efficiency solar cells.

However, a decreased in conductivity was observed for the BiOI films when annealing temperatures $\geq 450$ °C were applied. This is probably due to the material breakdown, oxidation, sublimation of the layer at higher annealing temperature and diffusion of Na from glass to BiOI layer. This trend is also consistent with the thickness measurement, which demonstrates the loss of material, hence reducing BiOI thickness after being annealed $\geq 450$ °C and causing the presence of shattered flakes microstructure for the sample annealed at 550 °C (figures 4(c) and 5(e)). Furthermore, many researchers have reported that the diffusion coefficient of Bi depends on several factors such as its composition, impurities, annealing temperature, time and environment [16, 17, 24]. With this observation, we postulate that heat treatment temperature above 450 °C is close to the activation enthalpy point for bismuth out-diffusion.

**ii. Structural effect in the electrical properties**

The structural study showed an improvement of crystallinity with annealing temperature, where this parameter has a significant effect on electrical conductivity. The XRD patterns of the as-deposited and annealed
BiOI layers are shown in figure 6. BiOI films for as-deposited and annealed at 250 and 350 °C are single crystalline with tetragonal structure along with four distinct and intense peaks 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 same trend has been observed by other researchers [9, 19, 20]. The highly oriented growth of BiOI with crystal planes (102) and (110) represents the flakes oriented perpendicular to the surface. The peak intensity of BiOI has gradually increased from as-deposited to after annealed at 350 °C, indicating the formation of highly crystalline products. Annealing treatment on BiOI film has initiated the crystal growth by producing the larger crystallites number. The enhancement of crystallinity further reduces the active defect states that act as electron traps in a band gap, resulting in higher electron conductivity and slow recombination of electron-hole pairs [27].

XRD spectra for BiOI films annealed at temperature ≥450 °C show the appearance of new peaks of Bi$_5$O$_7$I$_3$ and Bi$_7$O$_9$I$_3$ at 2θ = 27.15° and 47.35° with an orthorhombic crystal structure. The appearance of new crystalline peaks is observed by two small peaks which belong to Bi$_5$O$_7$I$_3$ material with orthorhombic phase, suggesting that BiOI films annealed at temperature ≥450 °C could be either the mixture between tetragonal and orthorhombic. The extremely high annealing temperature could induce the phase transition from a single-crystalline to a polycrystalline structure. Grain boundary resistance is generally higher for polycrystalline materials even it has low impurity, homogeneous grain and good preparation materials. These boundaries are two-dimensional internal interfaces that have an atomic packing different from that of the single-crystal grains. This behaviour is illustrated in figure 7(b), where the bonds at the boundary between two crystal grains are strained, providing more resistance to carrier flow and degrading the electronic properties. Hence, polycrystalline materials generally have lower electrical conductivity in single crystals [28].

From this work, it is evident that the high annealing temperature deteriorates the crystallinity of the BiOI films. The highest crystallinity is observed for a sample annealed at the temperature of 350 °C. Therefore, the
findings suggested that the film has the highest order of atomic arrangement, which is homogenous and having more stoichiometry.

Conclusions

In this research, we report for the first time a systematic study of the electrical properties of BiOI grown from a synthesised aqueous medium using the SILAR technique at room temperature. Based on the results, it can be observed that the thickness, structural and microstructural characteristics of BiOI film had a vital role in improving the electrical conductivity of the material. The DC conductivity measurement showed that the conductivity increases as the annealing temperature increases due to the improvement in ordered phase, reduction of the defect states and grain boundaries, enlargement of the grain size and crystallinity, which promotes the higher mobility of charge carriers. However, the extremely high temperature and/or a prolonged duration in annealing deteriorate the BiOI films due to the particle’s aggregation, grains coalescence, loss of material through sublimation and formation of a polycrystalline structure with mixed phases, hence reduce the electronic properties and of tribological performance of BiOI films. Therefore, we suggest that 350 °C is an optimal processing temperature for BiOI thin films. All in all, this study has provided significant outputs and a pathway for non-toxic BiOI thin film for lead-free perovskite solar cells.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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