



Development of BiOI thin films for lead-free perovskite solar cells

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Abstract: Lead-free bismuth oxyiodide (BiOI) perovskite solar cells (PSCs) have been successfully fabricated with multilayer structure by successive ionic layer adsorption and reaction (SILAR) technique. The conductivity and microstructure of BiOI thin films under several heat treatment has been studied prior to the device fabrication. From SEM result, flower shaped flakes microstructure is obtained in as-deposited BiOI layer and it enlarged as the heat treatment increased up to 350°C, and afterward crushed with higher heat treatment temperature. This is associate with the trend in conductivity measurement where BiOI achieved the optimum conductivity when it was heat treated at 350°C and reduced as the heat treatment exceed 450°C. This could be due to the reduction of grain boundaries as a result of development of the flakes sizes during the heat treatment, material sublimation and particle aggregation that developed higher resistance in the BiOI layers. The device performance under optimum heat treatment has been characterized using I-V measurement under a solar spectrum simulator with AM 1.5 illuminations. BiOI PSCs treated at 350°C showed ~6% efficiency. This study provided better understanding on BiOI thin film behaviors under several heat treatments and its potential to be applied as lead-free PSCs.

Keywords: *Bismuth oxyiodide, lead-free perovskite solar cells*

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Nomenclature	
PSCs	Perovskite solar cells
BiOI	Bismuth oxyiodide
SILAR	Successive ionic layer adsorption and reaction
HTL	Hole-transport layer
ETL	Electron-transport layer
CBD	Chemical bath deposition
CIGS	Copper indium gallium selenide
ITO	Indium doped tin oxide
SEM	Scanning electron microscope

1. INTRODUCTION

PSCs are traditionally fabricated in a single bandgap device structure where an active layer (Pb-halide perovskite) is deposited in between of hole-transport layer (HTL) and electron-transport layer (ETL). This mechanism enables conventional device structures to be able to surpass efficiency of 20%. However, Pb is listed by the World Health Organization as among the chemicals of major public health and environmental concern, and its use is restricted under several legislations worldwide [1]. Thus the used of Pb-halide PSCs for large-scale development brought controversy within the scientific community.

Multiple studies have documented to use lead-free materials to replace the Pb in perovskite solar cells without negatively affecting their performance. Nevertheless, the lead-free PSCs demonstrate low efficiency with less than 4% due to the small output current and instability [2]. For example, Tin (Sn) halide perovskites can be considered an alternative material to Pb-halide perovskites, but their low current and unsteadiness impede the substitution of Sn-halide for Pb-halide perovskite. The study on Indium (In) has been initiated, but the commercial prospects of this alternative have been severely restricted as In-halide perovskites are volatile against reduction-oxidation circumstances. 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, E_g of $\sim 1.63\text{--}2.1$ eV [2-4]. BiOI thin film can be deposited using chemical bath deposition (CBD), spray pyrolysis and modified successive ionic layer adsorption and reaction (SILAR) [3, 5]. SILAR method will be used in this study because of the simplicity, repeatable and able to produce a uniform layer.

Research on multilayer perovskite has been developed by changing halide anion concentration and bandgap tuning of the perovskite absorber layer that deposited in between GaN as the electron transport layer and graphene aerogel as a hole transport layer [6]. This device structure produces stable and reproducible solar cells, but the PCE is still low. Another work on multi-junction tandem cells has been done using a tunable bandgap of methylammonium-lead-halide integrated with crystalline silicon and copper indium gallium selenide (CIGS). Still, it necessitates interconnection between the perovskite sub-cells and complicated electrical coupling, which causes electron-hole recombination centers. Here, we proposed good efficiency of multilayer lead-free perovskite solar cells heat treated at optimum temperature based on the prior BiOI thin film characterization.

2. EXPERIMENTAL METHOD

BiOI thin film was deposited using SILAR technique. In order to start the synthesise solution, two beakers, with each contained 50 ml of deionized water were prepared. The first beaker is added with 0.5 M of bismuth (III) nitrate ($\text{Bi}(\text{NO}_3)_3$) while another beaker is added 0.5 M potassium iodide (KI). Both solutions were stirred for 30 minutes. The third beaker contained deionized water was prepared as the rinse bath. Glass/indium doped tin oxide (ITO)/TO substrate was used as substrate in this work. It was clean thoroughly before the coating process. The coating process started with initially dipped the glass/ITO into the first beaker for 10 s and straight dipped to the second beaker for chemical reaction for 20 s. Finally, the glass/ITO was dipped in the third beaker and rinsed to complete one cycle dipping process. During the dipping process, the substrate was positioned inclined in the beaker. The dipping cycle process was repeated for 30 times to obtained a decent layer.

The deposited BiOI layers were heat treated at various temperature starting from 250° , 350° , 450° and 550° C. The conductivity of BiOI film has been studied through four-probe hall effect measurement while the microstructural of BiOI thin films have been characterized using scanning electron microscope (SEM).

The optimum BiOI thin film was then applied as an active layer in PSCs with the device structure glass/ITO/ TiO_2 /BiOI/spiro-OMeTAD/Au. Figure 1 shows the schematic of the fabricated BiOI lead-free perovskite solar cells. An ETL consists of TiO_2 thin film and it has deposited on a glass/ITO substrate followed by three layers of BiOI with different concentrations ration of iodine to bismuth. BiOI layer with half concentration ratio of iodine to bismuth named as BiOI 0.5 is deposited as first perovskite layer. The second perovskite layer comprises the BiOI layer with an equal concentration ratio of iodine to bismuth named BiOI 1.0. Finally, the third perovskite layer is BiOI with a double concentration ratio of iodine to bismuth, named iodine BiOI 2.0. All the perovskite layers are deposited using SILAR dip-coating, and the total thickness for each layer is from 500 - 800 nm. The HTL consists of a spiro-OMeTAD and it was grown using spin coating followed by the top electrode comprises a layer of gold (Au). Conductivity and microstructure of active layer was studied prior the device development. The fabricated device was measured using I-V measurement under a solar spectrum simulator with AM 1.5 illuminations.

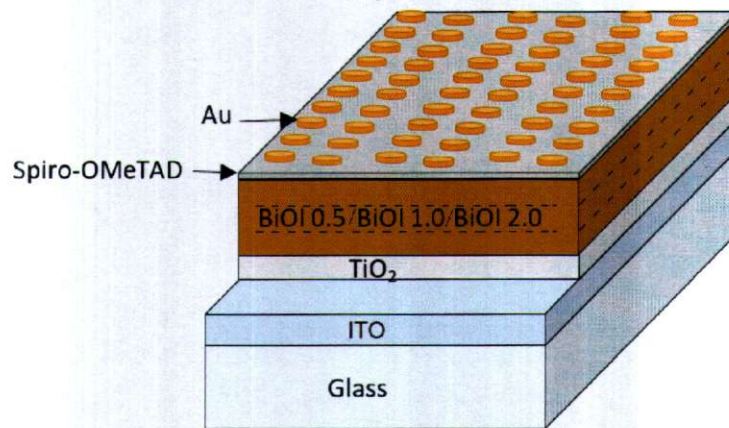


Figure 1 BiOI PSCs device structure.

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3. RESULTS AND DISCUSSION

A. Thin Film Characterization

The average resistance of FTO/BiOI/Au structures were measured using I-V characteristics. The electrical conductivity was calculated with known thicknesses of the BiOI layer. The graph of the conductivity versus annealing temperatures is presented in Figure 2. Also, the scanning electron microscope (SEM) images for as-deposited BiOI thin films and after annealed at 350°C and 550°C was added in the inset of Figure 2.

It is observed that the electrical conductivity of BiOI film decreased slightly as it was annealed at 250°C compared to the as-deposited layer. The conductivity increased from 2.68×10^6 to $1.63 \times 10^4 \text{ Sm}^{-1}$ and achieved the highest peak after annealed at 350°C. The conductivity enhancement is due to the improvement of crystallinity, the enlargement of the flakes size and the reduction of defects which promote the higher mobility of electrons [7]. As shown in Figure 2(a), the as-deposited BiOI film consists of agglomerations of flakes with flower shape. Due to the agglomerations, the electrons suffer grain boundary scattering when traveling in both direction, parallel and vertical to the substrate. Therefore, the measured conductivity is fairly low. During annealing process, these agglomerations and smaller flakes increase from $\sim 0.8 \mu\text{m}$ to $\sim 3.2 \mu\text{m}$ after annealed at 350°C as shown by the SEM images in the inset of Figure 2(b). Thus, the electrons can move along the fully crystalline grains from the ITO to Au contacts and there are no grain boundaries to hinder the charge carrier movements. This shows the benefits of having micro-size columnar type flakes in solar cell. In addition to this high conductivity, the larger flakes microstructure introduces active 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 transfer of electrons and holes in different paths and minimise the recombination [6]. This will provide the future research direction for producing high efficiency solar cells.

However, a decreased in conductivity was observed for the BiOI films at annealing temperatures $\geq 450^\circ\text{C}$. 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 reduced BiOI thickness after annealed $\geq 450^\circ\text{C}$ and SEM image inserted in Figure 2(c) that displays the shattered flakes microstructure for sample annealed at 550°C. Also, many have reported that the diffusion coefficient of Bi depends on several factors such as its composition, impurities, annealing temperature, time and environment [6-7]. With this observation we believed that heat treatment temperature above 450°C is closed to the activation enthalpy point for bismuth out-diffusion.

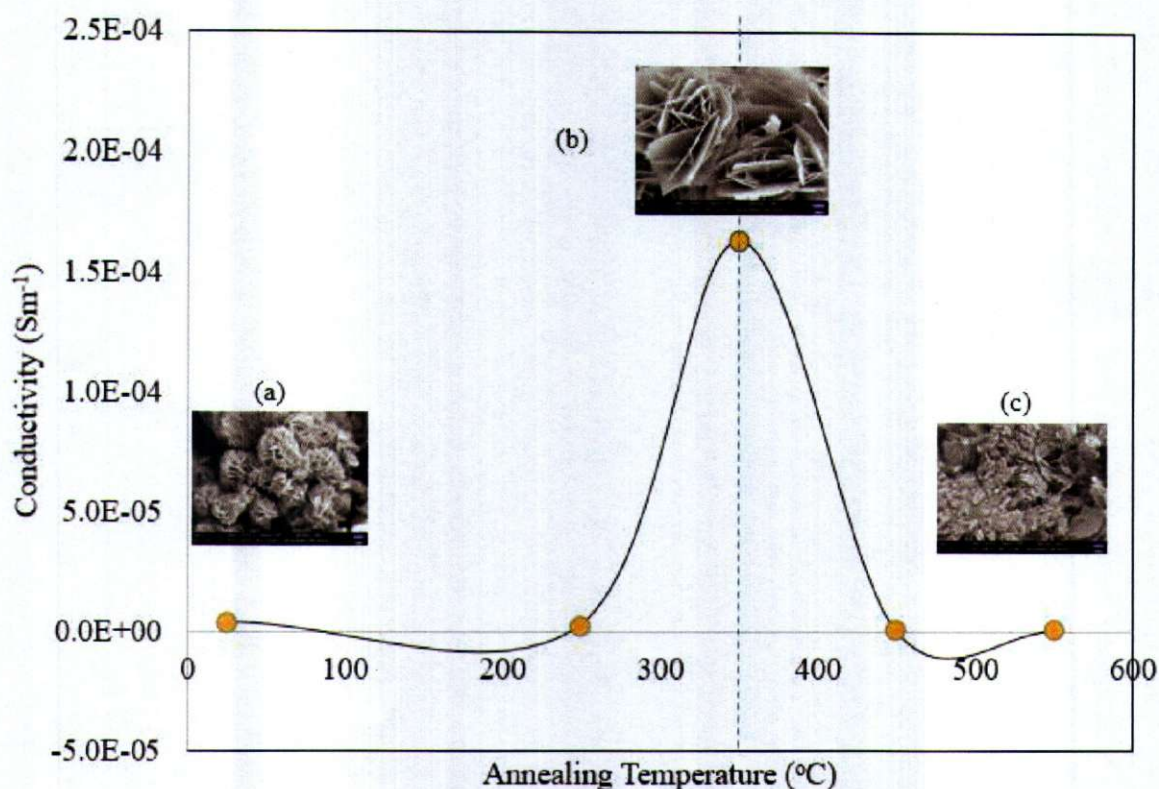


Figure 2: The conductivity measurements of BiOI for as-deposited and at various annealing temperatures. The inserted figure is SEM image of (a) as-deposited and annealed BiOI films at (b) 350°C and (c) 550°C.

B. Solar Cell Measurement.

Figure 3 shows the response characteristic of perovskite solar cells for BiOI layer heat treat at 350°C. The current density, J_{sc} , open circuit voltage, V_{oc} and good efficiency were observed with $\sim 28.3 \text{ mAcm}^{-2}$, $\sim 0.62 \text{ V}$ and $\sim 6\%$, respectively. The heat treatment at 350°C has been chosen based on the optimum characteristic from conductivity and microstructure measurement. Heat treat is vital in solar cell fabrication. From prior material study, it is believed that the heat treatment at 350°C could improved a solar cell device due to the strong built-in electric field that enhances the separation of the charge carriers, speeds up the photo-generated electron to the bottom electrode (ITO), and transfers holes to the top electrode (Au) with little or no recombination.

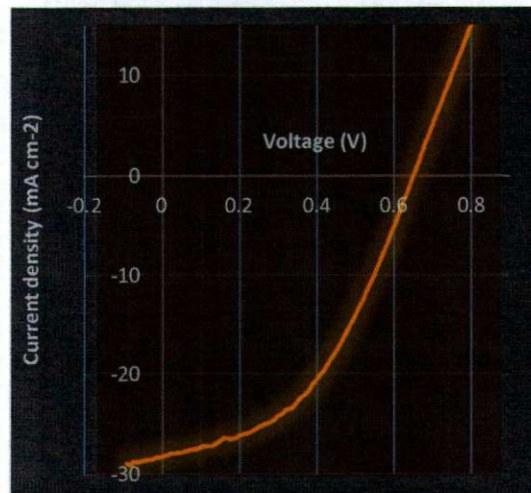


Figure 3. J-V characteristic of BiOI PSCs heat treated at 350°C.

4. CONCLUSION

From this work, it is evident that the high annealing temperature deteriorates the microstructure of the BiOI films. The optimum BiOI film was observed for a sample annealed at the temperature of 350°C. Therefore, the findings suggested that the device treated at this temperature shows the best efficiency since the active layer has the highest order of atomic arrangement, which is homogenous and having more stoichiometry.

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