ENHANCEMENT OF LEAD-FREE PEROVSKITE SOLAR CELLS DEVICES BY HEAT TREATED BISMUTH OXYIODIDE THIN FILMS

Nor Azlian Abdul Manaf[1], Asyraf Hakimi Azmi[1], Salmiah Ibrahim[2] and Fijay Fauzi[3]

[1]Physics Department, Centre for Defence Foundation Studies, National Defence University of Malaysia, Sungai Besi Camp, 57000 Kuala Lumpur, Malaysia.

[2]Physics Department, University of Malaya, 50603 Kuala Lumpur, Malaysia.

[3]Faculty of Electrical Engineering, University Malaysia Perlis, Pauh Putra Campus, 02600 Arau, Perlis, Malaysia.

Abstract.
Lead-free bismuth oxyiodide (BiOI) perovskite solar cells (PSCs) have been successfully fabricated using successive ionic layer adsorption and reaction (SILAR) technique. The effects of heat treatment temperature on thickness, conductivity and microstructure of BiOI thin films have 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 crushed with higher heat treatment temperature, afterward. This is associated 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 exceeded 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 particles aggregations that developed higher resistance in the BiOI layers. The devices performances under optimum heat treatments have 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, heat treatment, lead-free perovskite solar cells

1. INTRODUCTION

Perovskite solar cells (PSCs) based on lead halide (Pb-halide) has attracted much attention because of their high efficiency approaching the highest record of polycrystalline silicone modules. However, Pb-halide PSCs has brought controversial within the scientific community since 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]. 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 ~1.63–2.1 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 BiOI thin films largely focused on characterization and optimization of the physical and materials properties and its application in photovoltaics. However, there has been little attention on the effect of heat treatment on the conductivity characterization and photo-response characteristics. There are quite a few reports on fabrication of BiOI PSCs and its characterization. Putri et al. reported the improvement of photovoltaic performance was given by raised the heat treatment up to 300°C [6]. It was found that the heat treatment in between 100 to 400°C could result in phase transformation and structural change but with further temperature could cause iodine-deficient bismuth-based materials [6,7]. However, the effect of heat treatment on device parameters such as open circuit voltage, V_{oc}, short circuit current density, J_{sc} and efficiency of BiOI films still not documented. In the current work, BiOI thin films were prepared on glass substrates and heat treated at different temperature in the range of 250°C to 550°C to enhance its conductivity and optimize their property for PSCs application.

2. EXPERIMENTAL METHOD

BiOI thin film was deposited using SILAR technique. In order to start the synthesize 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 ($Bi(NO_3)$) 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/fluorine doped tin oxide (FTO) 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 active layers were heat treated at various temperature starting from 250°C, 350°C, 450°C and 550°C. Conductivity, thickness and microstructure of active layer was studied prior the device development. The conductivity of BiOI film has been studied through four-probe hall effect measurement, thickness of films was measured using optical profilometer and 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. Fig 1 shows the schematic of the fabricated BiOI lead-free perovskite solar cells. The fabrication started by depositing TiO_2 thin film on a glass/FTO substrate as an electron transport layer (ETL) followed by BiOI active layers. The thickness of BiOI perovskite active layer is about 500 nm. Four solar cell devices have been prepared with same procedure but different heat treatment on active layer from 250°C, 350°C, 450°C and 550°C. One as-deposited sample was kept as reference in this study. The subsequent layer, a spiro-OMeTAD is acted as a hole transport layer (HTL) and was grown using spin coating on the top of active layer, followed by the deposition of gold (Au) as a top electrode. All the fabricated devices with various annealing temperatures were measured using I-V measurement under a solar spectrum simulator with AM 1.5 illuminations.

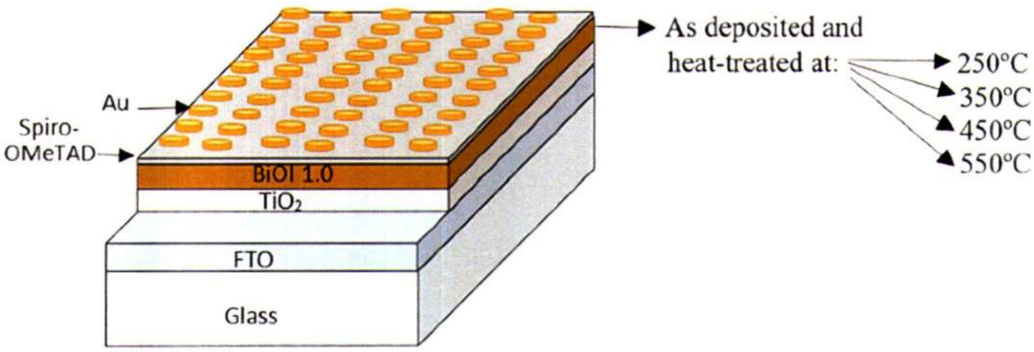

Fig 1. Solar cell device structure.

3. RESULTS AND DISCUSSION

A. Thin Film Characterization

The conductivity of FTO/BiOI/Au structures were measured using I-V characteristics and calculated with known thicknesses of the BiOI layer. The graph of the conductivity and thickness versus heat treatments is presented in Fig 2 and the images of scanning electron microscope (SEM) for as-deposited BiOI thin films and after heat treated at 250°C, 350°C, 450°C and 550°C are shown in Fig 3. It is observed that the electrical conductivity of BiOI film decreased slightly as it was heat treated at 250°C compared to the as-deposited layer. The conductivity increased from 2.68×10^6 to 1.63×10^4 Sm^{-1} and achieved the highest peak after heat treated at 350°C. The conductivity enhancement associated with the SEM images that demonstrated the transformation and enlargement of the flakes that promotes the higher mobility of electrons [7,8]. The thickness of the as deposited BiOI film also increased slightly after it was heat treated at 250°C correspond to the enhancement on its crystallinity, porosity, surface and microstructure of the film. However, BiOI films are decreased from 8.80 μm (250°C) to ~6.51 μm when the samples heat treated at temperature up to 450°C. The thickness of BiOI film shows a rapid decline to almost half of the thickness (~3.48 μm) when it heat treated at 500°C, which can be attributed to shrinkage and densification of the thin films as the result of the particles aggregation and grains coalescence. As shown in Fig 3(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 heat treatment process, these agglomerations and smaller flakes transformed and increased from ~0.8 μm to ~1.7 μm after heat treated at 350°C as shown by the SEM images in Fig 3(c). Thus, the electrons can move along the fully crystalline flakes from the ITO to Au contacts and there are no flakes boundaries to hinder the charge carrier movements. In addition to this 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 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 heat treatment temperatures ≥450°C. This is probably due to the material breakdown, oxidation, sublimation of the layer at higher heat treatment temperature. This trend is also consistent with the thickness measurement which demonstrates the loss of material, hence reduced BiOI thickness after heat treated ≥450°C and SEM image inserted in Fig 2(c) that displays the shattered flakes microstructure for sample heat treated at 550°C. Also, many have reported that the diffusion coefficient of Bi depends on several factors such as its composition, impurities, heat treatment 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.

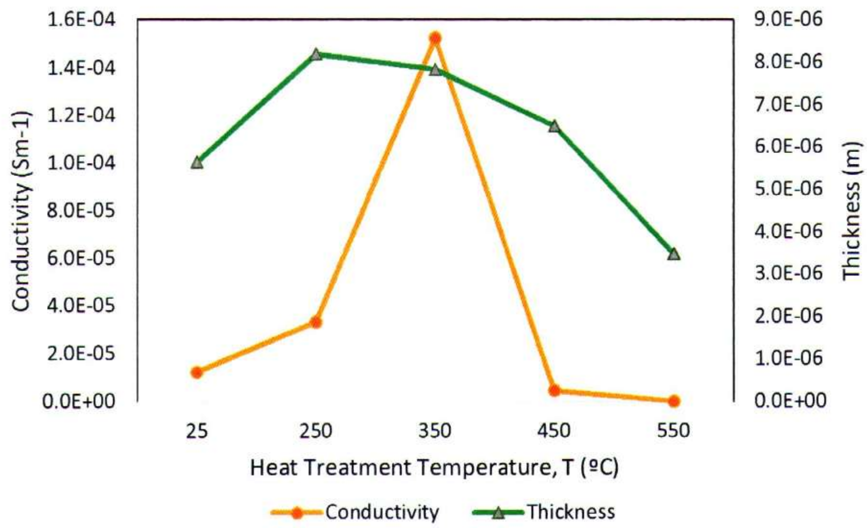

Fig 2: The conductivity and thickness measurements of BiOI for as-deposited and at various heat treatment temperatures.

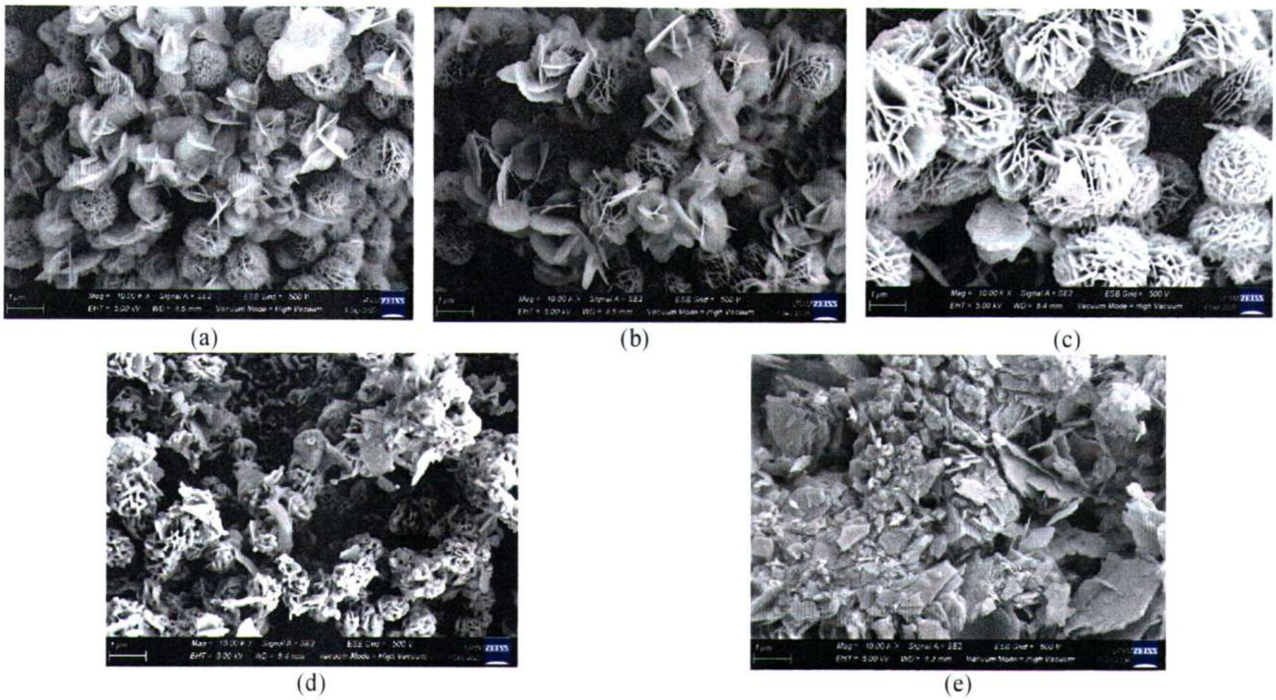

Fig 3: The SEM images of (a) as-deposited and heat treated BiOI films at (b) 250°C, (c) 350°C, (d) 450°C and (e) 550°C.

B. Solar Cell Measurement.

J-V characteristic for measurement under light of BiOI PSCs as deposited and heat treated at 250°C and 350°C is shown in Fig 4. It is observed that the as deposited PSCs generally low in short current density, J_{sc} and efficiency. The as-deposited BiOI layer is a highly defective material with residual impurities and numerous grain boundaries. Therefore, it needs an appropriate heat treatment process to enhance its properties for higher device performance. As the BiOI PSCs were heat treated the J_{sc}, open circuit voltage, V_{oc} and efficiency improved. However it is also spotted that PSCs reduced slightly after it was heat treated at 250°C. The formation of of small voids and gaps between the grain boundary in the SEM images could be the main reasons why the J_{sc} is low for this device. As the heat treatment temperature increased, the J_{sc}, V_{oc}, filled factor, *FF* and efficiency improved. In particular, device heat treated at 350 °C demonstrated the best performance with J_{sc} = ~16.8 mAcm^{-2}, V_{oc} = ~0.62 V and efficiency = ~4.1% compare to others. It shows that the attempt to heat treat BiOI PSCs at 450 °C and 550 °C is unsuscceeful. This result is due to the deterioration of BiOI thin films as presented in SEM and conductivity measurement.

Heat treat is vital in solar cell fabrication. From material study, it is believed that the heat treatment at 350°C could improved a solar cell device due to the improvent in electron mobility and micro-crystal stucture in device due to the higher conductivity and electron mobility field that speeds up the photo-generated electron to the bottom electrode (ITO), and transfers holes to the top electrode (Au) with little or no recombination.

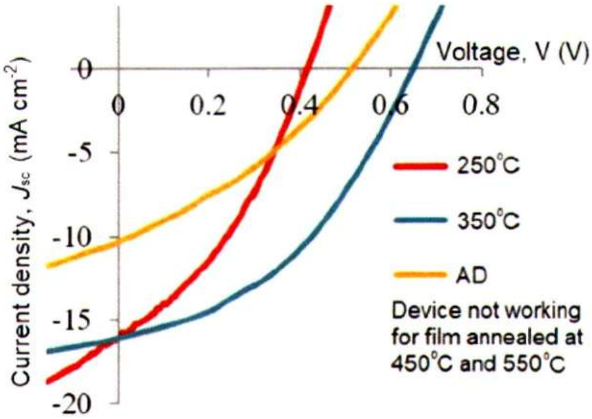

Fig 4. *J-V* characteristic of BiOI PSCs for as deposited and heat treated at 250°C and 350°C.

4. CONCLUSION

From this work, it is evident that the high heat treatment temperature deteriorates the microstructure of the BiOI films. The optimum BiOI film and BiOI PSCs performance were observed for a sample heat treated 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.

Acknowledgment

The authors would like to thank Ministry of Higher Education for the Fundamental Research Grant Scheme (FRGS) FRGS/1/2019/STG07/UPNM/02/3.

REFERENCES

1. P. Su, Y. Liu, J. Zhang, C. Chen, B. Yang, C. Zhang, X. Zhao, *J. Phys. Chem. Lett.*, 11, 8 (2020)
2. J. P. Correa-Baena, M. Saliba, T. Buonassisi, M. Grätzel, A. Abate, W. Tress and A. Hagfeldt, 358:6364, 739 (2007).
3. A. Kariper, *Mater. Res.*, 19, 1 (2016).
4. J. Di, J. Xia, H. Li, S. Guo, S. Dai, *Nano Energy*, 41, 172-192 (2017).
5. A. Abuelwafa, R. M. D. Matiur, A. A. Putri, T. Soga, *Optical Materials*, 109, 110413 (2020).
6. A. A. Putri, S. Kato, N. Kishi and T. Soga, *Applied Sciences*, 9, 3342 (2019).
7. N. A. Abdul-Manaf, A. H. Azmi, F. Fauzi and N. S. Mohamed, *Material Research Express*, 8, 096401 (2010).
8. H. S. Kim, A. Hagfeldt, N. G. Park, *Chemical Communications*, 55:9, 1192-1200, (2019).