THIN FILM SOLAR CELLS BASED ON BISMUTH OXYIODIDE

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ABSTRACT

Perovskite solar cells (PSCs) have drawn a lot of attention among scientific community because their power conversion efficiency (PCE) is comparable to crystal silicon solar cells. The conventional PSCs are using Pb-based halide perovskites, but the presence of Pb in these devices has caused some concerns due to the high perceived toxicity and hinder the pace of commercialization. Therefore, in this work we developed a Pb-free perovskite material based on bismuth oxyiodide (BiOI) thin films to replace Pb-halide PSCs. BiOI thin film has been grown by successive ionic layer adsorption and reaction (SILAR) dip coating. The films were heat-treated at 250°C, 350°C, 450°C and 550°C. Microstructure and electrical conductivity of BiOI were studied prior the device development through scanning electron microscope (SEM) and I-V measurement. The BiOI was then applied as an active layer in PSCs with the device structure glass/ITO/TiO_2/BiOI/spiro-OMeTAD/Au and heat treated at 250°C, 350°C, 450°C and 550°C. All the fabricated devices were measured using I-V measurement under a solar spectrum simulator with AM 1.5 illuminations. The SEM image shows the agglomerations of flakes for as-deposited sample. These agglomerations and smaller flakes increase from ~0.8 μm to ~3.2 μm after annealed at 350°C. The electrical conductivity of BiOI film increased from 2.68×10^{6} to 1.63×10^{4} Sm^{-1} and achieved the highest peak after annealed at 350°C due to the improvement of crystallinity, the enlargement of the flakes size and the reduction of defects which promote the higher mobility of electrons. PSC device heat treated at 350°C demonstrated the best performance with J_{sc} = ~16.8 $mAcm^{-2}$, V_{oc} = 0.62 V and efficiency 6.1% compare to others.

Keywords: perovskite solar cells, bismuth oxyiodide

Themes: Materials for Devices

Introduction

PSCs are traditionally fabricated in a single bandgap device structure where an active layer, lead-halide 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 recorded by the World Health Organization as a pollutant and chemical known to caused birth defect and cancer along with 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 findings 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. 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 [2]. BiOI has high quality state of motion of electronics field in an electrostatic field and high tolerance in defect, similar with conventional Pb-halide. The theoretical Shockley-Queisser Limit (SQL) of BiOI is 22% showing its potential to compete conventional PSCs with proper research and development [3-5]. BiOI thin films can be grown using many techniques, but among these, modified successive ionic layer adsorption and reaction (SILAR) is more practical since it can produce highly reliable and repeatable uniform thin film.

Research on graded bandgap perovskite has been developed by changing halide anion concentration and bandgap tuning of the perovskite absorber layer that deposited in between gallium nitride (GaN) as the ETL and graphene aerogel as a HTL. This device structure produces stable and reproducible solar cells, but the PCE is still low [5]. 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) [6]. 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 graded bandgap lead-free perovskite solar cells heat treated at optimum temperature based on the prior BiOI thin film characterization [7].

Experimental Method

BiOI thin film was deposited using SILAR technique. In order to start the synthesis of the solution, two beakers, with each contained 50 ml of deionized water were prepared. The first beaker was added with 0.5 M of bismuth (III) nitrate ($Bi(NO_3)$) while another beaker was added with 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/ITO 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 (I: Bi = 0.5: 1.0) 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 (I: Bi = 1.0: 1.0) named BiOI 1.0. Finally, the third perovskite layer is BiOI with a double concentration ratio of iodine to bismuth (I: Bi = 2.0: 1.0), 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.

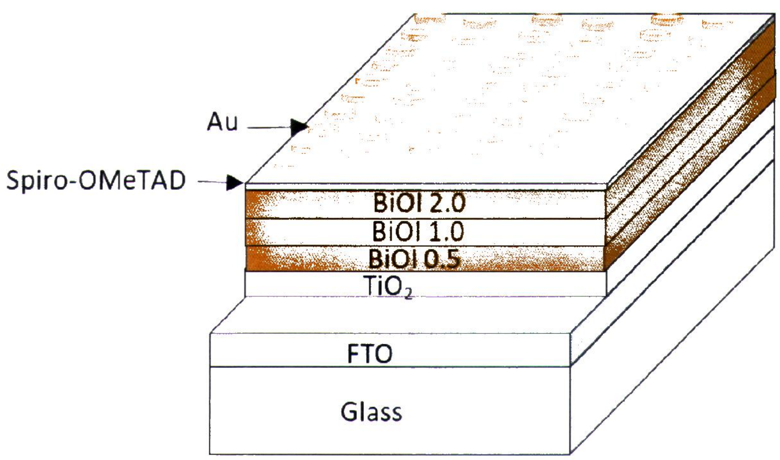

Figure 1: BiOI PSCs device structure.

Results and Discussion

Thin Film Characterization.

The electrical conductivity of BiOI thin films under several heat treatments were calculated from the average resistance obtained from I-V measurement and shown in Figure 2. The SEM images of as-deposited BiOI layer and after heat treated at 250°C, 350°, 450°C and 550°C also inserted in Figure 2 for better assessment.

From the graph of conductivity versus heat treatment, it is noticed that the conductivity of as-deposited BiOI increased slightly after heat treated at 250°C. The conductivity continues increased drastically to its maximum value (1.63×10^{4} Sm^{-1}) as heat treatment temperature increased to 350°C. This trend is related with the enhancement of the flakes size shown by the SEM images in microstructural study. SEM image of as-deposited BiOI thin film in Figure 2(a) demonstrated small flakes agglomerations similar to flower shape. This agglomeration resisted the electron flows due to the grain boundary, thus the electrical conductivity in as-deposited BiOI is low. As the heat treatment increased from 250°C to 350°C, the flakes size enlarged as disclosed in Figure 2 (b) and (ca). From this, we can narrate that the improvement of BiOI conductivity is due to the enlargement of the flakes size that reduced the grain boundary, consequently enhanced the electron mobility in BiOI thin films [4-5].

This study proves the advantages of having micro size flakes or columnar in active layer of solar cells device. The BiOI thin film demonstrated the cutback of conductivity value as the samples were heat treated at 450°C and above. This trend is also associated with the microstructure studies presented by SEM images in Figure 2 (d) and (e). The SEM image of BiOI exposed the shattered flakes microstructure for samples heat treaed at 450°C and 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.

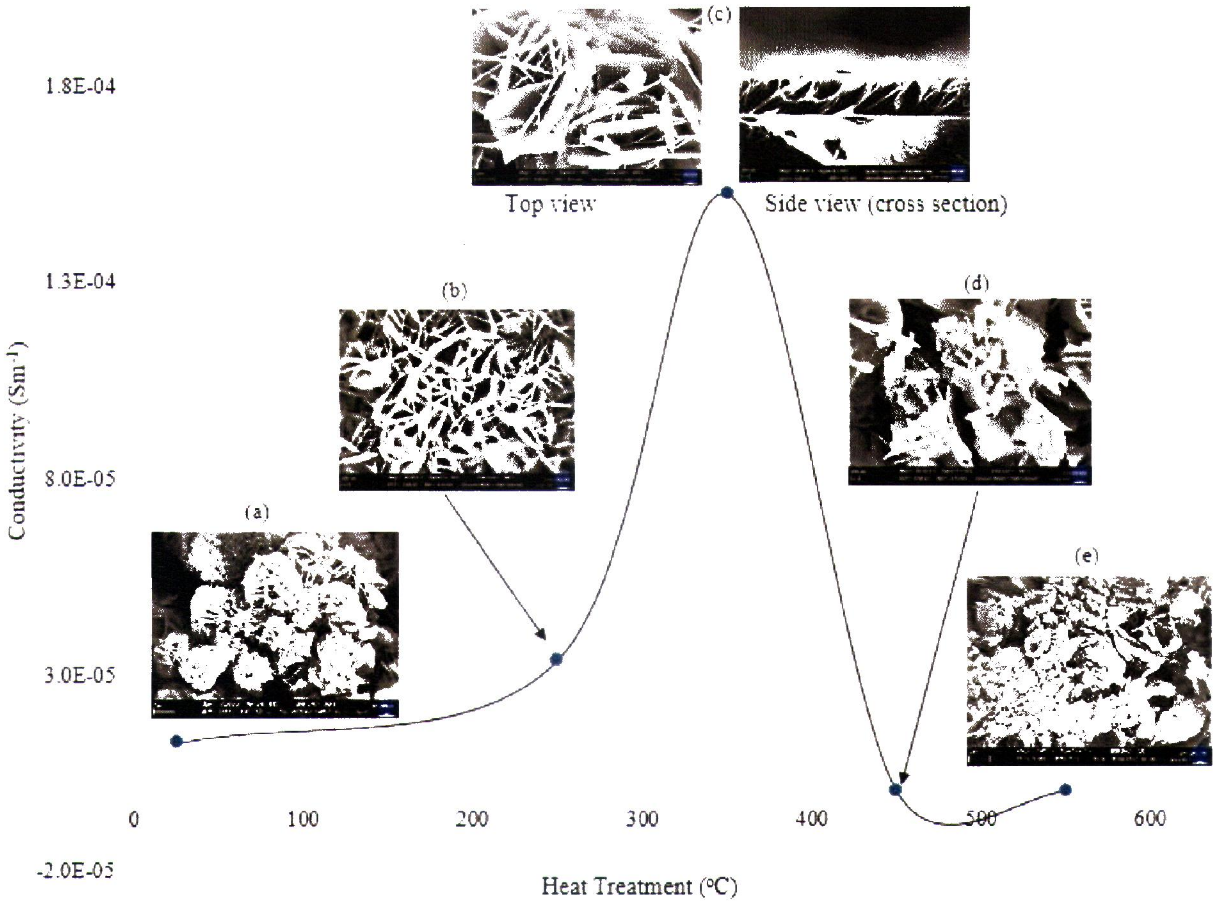

Figure 2: The graph of electrical conductivity versus heat treatment for BiOI thin films.The inserted figure are the SEM images of BiOI thin films for as deposited and heat treated at various temperatures.

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 ~28.3 $mAcm^{-2}$, ~0.62 V and ~6%, respectively. The heat treatment at 350°C has been choosen based on the optimum charateristic 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.

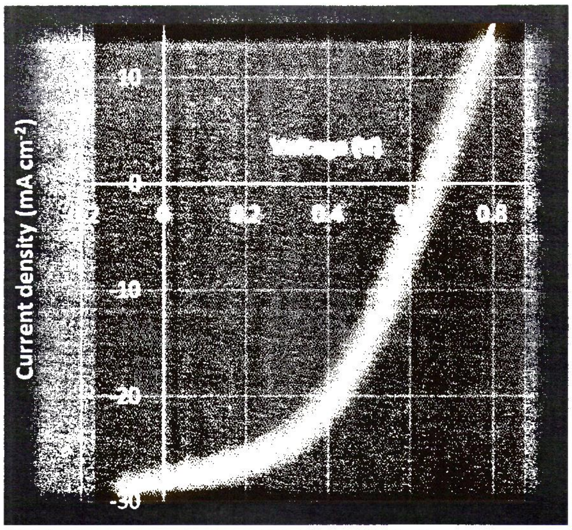

Figure 3. J-V characteristic of BiOI PSCs heat treated at 350°C.

Summary

BiOI thin film heat treated at 350°C shows the optimum performance based on its electrical conductivity and microstructural studies. The application of BiOI as an active layer in lead-free graded bandgap PSCs shows good efficiency of ~6%. This work gave better understanding on BiOI behavior under heat treatments process and established its potential as an alternative lead-free material to replace conventional lead-halide PSCs.

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