A simple spin-assisted SILAR of bismuth oxyiodide films preparation for photovoltaic application

Anissa A. Putri^{1,2} · Amr Attia Abuelwafa^{1,3} · Shinya Kato¹ · Naoki Kishi¹ · Tetsuo Soga¹

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Abstract

Bismuth oxyiodide (BiOI) films have been successfully fabricated from $\text{Bi}(\text{NO}_3)_3$ and KI precursors at room temperature via facile successive ionic layer adsorption and reaction assisted with spin-coating (spin-SILAR). In our work, the uniform and dense BiOI layer was easily formed in a shorter time by more environmentally friendly process. X-ray diffraction, Raman spectroscopy, and field emission scanning electron microscope (FESEM) were used to study the crystal structure and surface morphology of BiOI films. The absorption spectra in the UV–vis–NIR regions were also measured using spectrophotometric measurement in the wavelength range, from 300 to 2000 nm for clarifying the properties of resulted BiOI/FTO films. From the experiment, we obtained the short-circuit current density of BiOI films in the FTO/glass substrates which up to 0.612 mA/cm^2 . Although the superior solar cell performance was not exhibited by our BiOI films, due to the benefit of spin-SILAR method, it may open up the further application of BiOI films prepared through this method.

Keywords Thin films · BiOI · Spin-SILAR · Optical properties · Photovoltaic

1 Introduction

BiOI can be considered as the high-tolerant defect semiconductor material [1, 2] which is categorized as p-type semiconductor with the narrow bandgap at $\sim 1.8 \text{ eV}$. It has a strong absorption under the visible light irradiation [3, 4]. Owing to its character which is safe to the environment in comparison with the lead-based materials, BiOI has been commonly applied for photocatalytic reaction and photovoltaic devices [5–8]. Furthermore, BiOI can be successfully synthesized by successive ionic adsorption and reaction with dip-coating (dip-SILAR) [5, 8–10], chemical bath deposition (CBD) [11], chemical vapor transport [2, 12], mechanical grinding [13], and solvothermal reaction [6, 14]. Conventional dip-SILAR, CBD, and slip-casting from BiOI powder [15] are also common to obtain the BiOI films for photovoltaic application.

In the conventional dip-SILAR, the water rinsing should be included in all steps to maintain the film uniformity. Although good film quality can be acquired, this dip-SILAR consumes more time for producing the films due to the rinsing step. Therefore, it may be difficult to get more BiOI films in a shorter time. If the rinsing step in the dip-SILAR process is removed, the film uniformity may be poor although the dip-SILAR could be modified with different angles in its substrate direction [16]. Furthermore, it is considered that dip-SILAR has less reproducibility because it depends on the rinsing and dipping process even though it is low cost [17]. As we noticed that dip-coating is the most common method for preparing BiOI films, we tried to develop BiOI films preparation through a modified way, namely spin-coating method combined with SILAR (spin-SILAR) for the first time. This work was inspired by the Pb-perovskite synthesis and film preparation.

✉ Anissa A. Putri, anissaputri@walisongo.ac.id | ¹Department of Electrical and Mechanical Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan. ²Department of Chemistry, Walisongo State Islamic University, Semarang 50185, Indonesia. ³Nano & Thin Film Lab., Physics Department, Faculty of Science, South Valley University, Qena 83523, Egypt.

Spin-coating is the universal method for preparing films, such as P3HT, PEDOT, PSS, and perovskite material [18–20] for solar cell purposes. In spin-SILAR, this spin-coating method is combined with SILAR, in which its adsorption and reaction steps can occur while the spin-coating process is running. By utilizing this method, the rinsing step and drying process can be also completed when the solution is spun [21]. Then, we suppose that spin-SILAR can deposit flat BiOI films onto the substrates in a shorter time. In addition, only the small amount of precursor solution is required in spin-coating thanks to the less remaining waste solution in spin-SILAR. Due to this reason, it also offers the opportunity that spin-SILAR is more environmentally benign than dip-SILAR.

By the BiOI film deposition via spin-SILAR, we also studied the optical, physical, and photovoltaic properties of BiOI. We characterized the properties of deposited BiOI films via spin-SILAR by changing the number of cycles which follow the direction from the previous experiment [5]. Here, we found the uniformity of the resulted BiOI layer by spin-SILAR although the rinsing step was eliminated. Furthermore, the deposited BiOI films onto FTO/glass substrates could exhibit the performance of solar cell devices with Pt/FTO as counter electrode and I^-/I_3^- solution as electrolyte. We expect that this work can be a beneficial reference for BiOI exploration in BiOI solar cell development.

2 Materials and methods

2.1 Materials

We utilized $Bi(NO_3)_3 \cdot 5H_2O$ and KI which acted as the cation and anion sources that were purchased from Nacalai Tesque, Inc (Kyoto, Japan). The ultrapure water from Milli-Q direct water purification system with resistivity 18.2 MΩ·cm at 25 °C was used to make all the solutions during the research.

2.2 Deposition method

A total of 20 mg of $Bi(NO_3)_3 \cdot 5H_2O$ as bismuth source was dissolved in 5 mL deionized water, and the same mole ratio of KI as potassium source solution was also prepared for the initial materials. A sequential washing for three times in organic solvents, such as acetone (twice) and ethanol (once) for 5 min each, was carried out for glass substrates cleaning. It was followed by N_2 gas blowing and UV/ O_3 treatment for 30 min in total. To deposit BiOI films, each bismuth and potassium precursors were dropped separately onto the cleaned FTO glass substrates before spin-coating process. Moreover, spin-coating was

performed for 20 s at 1500 rpm. One cycle reaction is completed if a sequential dropwise addition of bismuth solution is followed by potassium solution dropping onto the substrates. The preparation of BiOI films by spin-SILAR method is illustrated in Fig. 1, and the number of cycles in this experiment was varied from 5 to 30 cycles. The thickness of the film was also estimated using cross-sectional image FESEM.

2.3 BiOI characterization and solar cell fabrication

The resulted films were characterized using X-Ray Diffraction (Rigaku RINT-2100 diffractometer), Raman Spectrometer (JASCO NRS-2100), FESEM JEOL JSM-7800F, and UV–visible Spectroscopy (JASCO 670 UV). Solar cell structure was prepared by a sandwich structure using FTO glass substrate, adapted from dye-sensitized solar cell devices without involving the dye solution [5]. The photovoltaic structure was arranged by FTO/BiOI photoanode and platinum based as a counter electrode, such as the cell: FTO/BiOI films/Iodine electrolyte/Pt-FTO. Then, this structure was tested using solar simulator (100 mW/cm²; AM 1.5 illumination) with 0.16 cm² of illumination area.

3 Results and discussion

3.1 Structural analysis

3.1.1 X-ray powder diffraction analysis

First, we studied the structural property of the prepared BiOI films by XRD analysis. The diffraction patterns of BiOI films using spin-SILAR for various cycles are shown in Fig. 2. The peaks in the diffractogram are in line with the BiOI crystal types in the JCPDS card 01-073-2062. It is obviously seen that the film crystallinity enhances due to the more reaction cycle. As to be expected, the further cycle will let the reaction take place to deposit BiOI crystal. In our films, only two types of BiOI crystal planes are

Fig. 1 Schematic diagram of spin-SILAR process for BiOI films preparation

Fig. 2 The XRD patterns of FTO and prepared FTO/BiOI films by spin-SILAR in the different reaction cycles: 5, 10, and 30 cycles

obtained via spin-SILAR, namely (001) and (102) planes which exist in 2θ at 9.76° and 29.6° . All the crystal patterns are dominated by the (001) crystal plane. Therefore, we assumed that the formation of BiOI crystal in our work was initiated by (001) plane growth. The amount of solvent can control the precursor acidity which leads to the change in the mechanism and kinetics of crystal growth. In BiOI synthesis, the crystal orientation can be different due to the distinct treatment and condition in the film preparation. By involving the Debye–Scherrer equation in Eq. 1 [22],

$$L = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where K is 0.94; λ is Cu wavelength (0.154 nm); full width at half maximum (FWHM) value (β) and Bragg angle (θ) in radian, we calculated the BiOI spin-SILAR crystallite size (L). In this work, we obtained the crystallite size of BiOI from 15 and 30 cycles of spin-SILAR which were around 13.95 and 14.78 nm. The smaller crystal size could be obtained from the spin-coated BiOI sample in the less cycle, such as in the BiOI film from ten cycles.

3.1.2 Raman study

For more exploration about BiOI structural properties, an investigation using Raman spectroscopy was carried out for the same samples. Figure 3 shows the BiOI character in Raman spectra. All the attributed peaks in this figure correspond to the E_g stretching mode of Bi-I vibration in BiOI. Although the impurity is not found in the Raman spectra, we observed that there is the Raman peak shifting. Generally, BiOI with (110) crystal peak has the E_g peak

Fig. 3 Raman spectra of the obtained BiOI films from spin-SILAR in the different reaction cycles: 5, 10, 15, 20, and 30 cycles

around $147\text{--}149\text{ cm}^{-1}$ [23, 24]. However, our BiOI via spin-coating process shifts to the E_g position 150.06 cm^{-1} after 15 cycles. This peak position for BiOI character was also reported for BiOI Raman spectra with the stronger peak crystal plane in (001) [25].

In addition, the BiOI formation follows the chemical reaction in Eq. 2 [26]. It occurs after the hydrolysis of bismuth precursor. The (001) crystal plane domination can be formed under the strong acidity situation. Otherwise, (110) crystal plane is easier to be obtained under the less acidic solution. If more water is added, the less concentration of $\text{Bi}(\text{NO}_3)_3$ can induce the hydrolysis rate acceleration. As a consequence, the nucleation rate will increase and promote the rapid growth of the crystal along with the (001) surface [6].

3.1.3 Surface morphology

By the FESEM analysis, we found that the 30 cycles of BiOI film had a dense and compact film in comparison with the dip-SILAR result [16, 27]. A more uniform flake-like structure could be obtained by this experiment as shown in Fig. 4. We identified that our flaky structure is the same as the obtained morphology of prepared BiOI by other researchers. Flaky BiOI is considered as the basic shape of BiOI, and sometimes, it can be in the sheet-like material [15]. When the cycle reaction increases during the film preparation, it can result in the bigger flaky size of BiOI material which is shown by the lateral size of BiOI flake in

Fig. 4 Top view of BiOI film FESEM images for: 10 cycles (**a**), 15 cycles (**b**), 30 cycles (**c**), and tilted image of BiOI film via spin-SILAR 30 cycles (**d**)

the films (see Fig. 4a–c). After 30 reaction cycles were finished, the BiOI films formed the bigger flaky morphology (Fig. 4c). However, its lateral size was half of the resulted BiOI by dip-coating, around 300 nm with the flake thickness around 10 nm [16]. The dip-coating process without rinsing step might also initiate further reaction between the remained BiO^+ in the substrate and iodide ion which induced in bigger BiOI growth, as shown in the previous report [16, 27].

By the tilting cross-sectional image, the more compact BiOI film by spin-coating is confirmed as shown in Fig. 4d, which tends to be denser than the previous dip-coated BiOI result [16, 27]. Owing to its smaller size, we predict that the prepared BiOI from spin-coating may have the

higher surface area which can be expected to result in the better performance for photocatalysis or solar cell application with the suitable hole and electron transport materials. The more uniform films in this work can be a good point of SILAR method without rinsing treatment assisted with spin-coating. Besides, it is easy to produce BiOI via spin-SILAR, and the films can be deposited by the reaction of spread solution onto the FTO substrate.

3.2 Optical properties

The optical study in Fig. 5a shows the absorption spectra, $A(\lambda)$ for BiOI/FTO system in UV–vis–NIR regions. The wider visible absorption of BiOI films due to the different cycles

Fig. 5 UV–visible absorbance (a), transmittance (b), and reflectance spectra (c) of prepared BiOI films by spin-SILAR in the different reaction cycles: 10, 15, 20, and 30 cycles

also can be reflected by the transmittance (see Fig. 5b) and reflectance spectra (see Fig. 5c). The greater film thickness and size of BiOI materials should have an impact not only on the decrease in transmittance spectra, but also on the longer shifting in its absorption edge, as shown in Fig. 5a, b and reported research [28]. Owing to the grain size increment, the film thickness will improve and lead to the maximum wavelength shifting [29]. The variation of the absorption coefficient with the photon energy is also given by Tauc's relation [30]:

$$\alpha h\nu = B(h\nu - E_g^{\text{Opt}})^r \quad (3)$$

Here, B is a parameter that depends on the transition probability, α is the absorption coefficient, E_g^{Opt} is the optical bandgap, and r is a number which characterizes the transition process, then $r = 1/2$ and $r = 2$ for direct allowed

and indirect allowed transitions, respectively. The best fitting of the experimental data to Eq. 3 is obtained when $r = 2$, so that, the type of electronic transition is indirect allowed transition, which is illustrated in Fig. 6. Our calculated E_g^{Opt} is in the range of BiOI bandgap energy [31]. We noticed that the bandgap estimation shows the change in the bandgap energy value among the resulted BiOI films. However, since the resulted film by five cycles of spin-SILAR was very thin, it was difficult to calculate its bandgap energy. Therefore, we cannot show the calculated bandgap energy from five cycles BiOI.

The bandgap energy evaluation of BiOI films can be arranged for the following order: 30 cycles (1.95 eV) < 20 cycles (1.95 eV) < 15 cycles (2 eV) < 10 cycles (2.25 eV). The bandgap energy values were less than those in the prepared films by dip-coating. The different sizes may be the reason for this matter since the bigger size could be

Fig. 6 The bandgap energy calculation of the prepared BiOI films by spin-SILAR in the different reaction cycles: 10, 15, 20, and 30 cycles

obtained in the thickening of films, and it changes the bandgap energy. The increase in particle size in our thin film may decrease the bandgap energy since the improvement in thickness and material growth can be generated along with the more reaction cycle. The crystal size reduction has impact on the bandgap energy value. Moreover, the different bandgap energies may be influenced by the different lattice strains, dislocation of film densities, and crystallite size of semiconductor materials.

Related to the increasing of thickness, it also has a correlation with the Raman spectra. The peak intensity of BiOI in the Raman spectra (Fig. 3) shows an increment due to the increasing of SILAR's cycle reaction number. The highest intensity of BiOI films is shown by the film from 30 reaction cycles via spin-SILAR. Hence, height intensity peak can also reflect its concentration which is in line with its film thickness.

3.3 Photovoltaic cell measurement

BiOI films can exhibit the IV performance although it has low efficiency of solar cell in comparison with the lead perovskite-based materials. We obtained more than $600 \mu\text{A}/\text{cm}^2$ of J_{sc} , while the reported FTO/BiOI films by conventional SILAR had the maximum J_{sc} of $260 \mu\text{A}/\text{cm}^2$ [5]. The solar cell evaluation by involving the iodine electrolyte with the structure FTO/BiOI/Iodine/Pt-FTO shows the data (Fig. 7 and Table 1). The more BiOI film in the solar cell exhibits higher solar cell parameter although it performed the decrease in its performance after 15 cycles, as shown in Fig. 8. This trend is similar to the previous work [9]. In our work, the best short-circuit current and open-circuit voltage were performed by

Fig. 7 I - V curve prepared BiOI films from spin-SILAR in the different reaction cycles: 5, 10, 15, 20, and 30 cycles

BiOI film from 15 cycles. By increasing the cycles, there was an impact on the increase in its open-circuit voltage. However, the shunt resistance and series resistance calculation (R_{sh} and R_s) indicated that due to the small R_{sh} value in the thicker BiOI films after 15 cycles, the V_{oc} values were lowered. The increasing of R_s value in BiOI films after 15 cycles also caused the drop in the short-circuit current. In solar cell, the voltage and current drops can be initiated by the decrease and increase in the R_{sh} and R_s values since the presence of R_{sh} will make another current path appear in the cell which reduces the common current flowing and its voltage.

In addition, the centrifugal force in the spin-coating might play an important role to accelerate the solvent evaporation. Therefore, the density of BiOI films in the FTO substrates can be completed by spin-SILAR. We pointed that the more (001) plane in the BiOI may be unpleasant for solar cell application since the solar cell performance declines due to the film thickening and (001) intensity increment. Since the different crystal type has the influence in the charge photogeneration, it may have the impact on the solar cell performance and the photocatalytic activity of BiOI [26] in comparison with the previous results [16, 27]. For future work, it may be possible to tailor the facet orientation in BiOI films via spin-SILAR and to study experimentally the effect of facet orientation of BiOI which is more favorable for solar cell application.

4 Conclusion

In this work, spin-SILAR was proposed for the growth of BiOI films for the first time, and by the solar cell analysis, it achieved the best solar cell parameters of $612 \mu\text{A}/\text{cm}^2$,

Table 1 Photovoltaic performance of BiOI films prepared from spin-SILAR in the different reaction cycles: 5, 10, 15, 20, and 30 cycles

Sample	Jsc (mA/cm ²)	Voc (V)	FF	Efficiency (%)	Rsh (10 ³ × Ω cm ²)	Rs (10 ³ × Ω cm ²)
Spin- 5 cy	0.334	0.365	0.361	0.044	19.69	0.127
Spin- 10 cy	0.375	0.391	0.385	0.056	21.03	0.116
Spin- 15 cy	0.612	0.446	0.378	0.103	31.11	0.112
Spin- 20 cy	0.470	0.431	0.360	0.073	25.56	0.123
Spin- 30 cy	0.271	0.419	0.427	0.048	24.24	0.122

Fig. 8 Short-circuit current and open-circuit voltage (a); and fill factor and efficiency (b) plots of prepared FTO/BiOI films from spin-SILAR in the different reaction cycles: 5, 10, 15, 20, and 30 cycles

0.446 V, and 0.103% for its Jsc, Voc, and PCE, respectively. Good quality of BiOI film can be obtained by SILAR assisted with spin-coating process although the washing step was eliminated. Due to the less time needed for films preparation and its simplicity, it is considered that this method can be aimed to prepare BiOI films for wider application. The crystal quality and quantity in the resulted BiOI films could be modified by the different preparation techniques. To sum up, the SILAR process assisted with the spin-coating could be an alternative way to produce BiOI films, whereas the number of reaction cycles in SILAR resulted in the different solar cell parameters. For the future work, the

developed BiOI films prepared by spin-SILAR for solar cell application can be attempted owing to the fact that it has the better compactness over the dip-SILAR result.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interest.

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