



Chiang Mai J. Sci. 2018; 45(5) : 1995-2004

<http://epg.science.cmu.ac.th/ejournal/>

Contributed Paper

High Photocurrent Gain of Spherical Nano-crystalline ZnO:Bi Film for Advanced Solar Cells Application

Peerawoot Rattanawichai [a], Thipwan Fangsuwannarak* [a], Rungrueang Phatthanakun [b] and Sirirat T. Rattanachan [c]

[a] School of Electrical Engineering, Institute of Engineering, Suranaree University of Technology, Nakhon Ratchasima, 30000, Thailand.

[b] BL6a: Deep X-ray Lithography, Synchrotron Light Research Institute (Public Organization), Nakhon Ratchasima 30000, Thailand.

[c] School of Ceramic Engineering, Institute of Engineering, Suranaree University of Technology, Nakhon Ratchasima, 30000, Thailand.

* Author for correspondence; e-mail: thipwan@g.sut.ac.th

Received: 1 November 2017

Accepted: 30 April 2018

ABSTRACT

Zinc oxide (ZnO) thin films are expected to have crucial applications in opto-electronic devices such as photo sensors, large-area displays and perovskite solar cells for an electron transport layer (ETL). In particular performance of nano-crystallinity for advanced photovoltaic (PV) cells, ZnO films have been very interested in recent years. However, their performances are not satisfactory at present: the photocurrent gain is quite low ($<10^2$ times more than dark current), the high reflectance R% is not beneficial to obtain high quality of PV cell, and the light-trapping enhancement on ZnO film has not yet been fully exploited in perovskite PV cells. Realizing high light-trapping and high photocurrent gain remain a big challenge today. In this paper, nano-crystalline zinc oxide films doped with bismuth (nc-ZnO:Bi) were synthesized through sol-gel processing and then formed by spin coating method. By adding the cation surfactant as cetyl trimethylammonium bromide (CTAB) in the sol-gel, good film quality and spherical nano-ZnO:Bi were obtained and performed at temperature annealing between 350-550C. Reflectance as low as 17% and transmittance (%T) of over 90% in the light wavelength between 390-800 nm, photoresponsivity values of 8 -28 A/mW and high photocurrent gain as high as 1×10^4 times comparing with dark current were achieved. The surface morphology of ZnO:Bi films with existence of spherical nano-particles with diameter size around 10-20 nm acts as light-trapping surface to improve photocurrent enhancement. Moreover, such high quality of their optical properties is able to contribute light-trapping performance of ETL for further emerging solar cells.

Keywords: ZnO:Bi film, spherical nano-crystal, emerging solar cells, electron transport layer, photocurrent gain, light-trapping

1. INTRODUCTION

Recently, zinc oxide is one of the most interesting materials for optoelectronic applications because of its highly effective electrical and optoelectronic properties. In particular its wurtzite crystal structure with wide direct energy band gap (~ 3.3 eV) and large excitation binding energy of ~ 60 meV can be verified at room temperature. ZnO nanostructures have been extensively studied over the past years owing to the availability of a variety of growth methods resulting in a number of different morphologies and a wide range of material properties [1]. In addition, ZnO nanostructures have very attracted intensive research effort due to high-performance micro-to-nanoscale optoelectronic devices such as transparent electronics, solar cells, photo catalysts, and chemical sensors [2-5].

Especially, additional ZnO thin film is a crucial nanostructure layer to improve electron transport in emerging perovskite solar cell. The availability of the generated electrons collecting at electrodes, light-trapping and their interfaces states are also critical for enhancement of its power conversion efficiency (PCE). The importance of the interface states properties has been revealed by electron induced current investigations, which show that efficient charge separation and collection to occur at the interfaces between the perovskite and both charge-selective layers [6]. The consideration of an effective material for operating as an electron transport layer (ETL) is important to achieve a high degree of charge selectivity. Meanwhile, ETL is able to maintain a low surface recombination to minimize energy loss at the heterojunction interfaces. A variety of ETL has been explored for achieving high-efficiency perovskite devices. Various metal oxides are the most common materials for ETL utilization. Wide band gap metal oxides,

such as ZnO have been used to fabricate the devices in the mesoscopic structure [7-9]. An electrically insulating mesoporous layer allows high open circuit voltage (V_{OC}) to be achieved if there is a lack of sub-band gap and surface electronic states [10]. Therefore, ZnO as an appropriate electron transport layer to improve the perovskite devices can provide many advantages, including high mobility and optimization processing temperature.

In addition, one of the most crucial advantages of ZnO is the variety of growth methods including rf magnetron sputtering [11], solution-based method which is simple and inexpensive [12], hydrothermal process which is low-temperature [13], spray pyrolysis [14], and co-precipitation method [15]. This further contributes to the intense interest in ZnO for emerging solar cell.

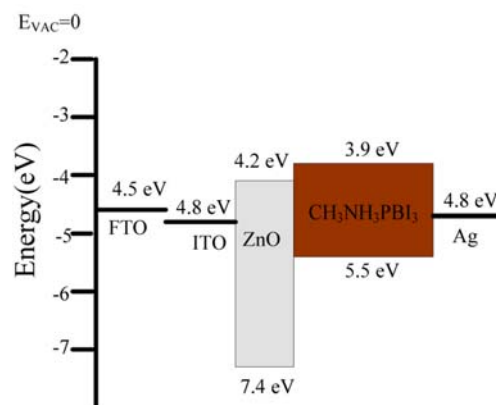


Figure 1. Energy alignment of ETL-free perovskite solar cells.

Figure 1 shows the interface energy alignment of electron transport layer (ETL) between free planar perovskite and transparent metal in solar structure (TCO/ZnO/CH₃NH₃

PbI₃/Ag). Another important role of ZnO plays as a n-type semiconductor material, which can generate photocurrent with large

energy gap, good conductivity of electrons and shallow conduction band edge level (4.2 eV), which matches well with the conduction band of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite (3.9 eV).

In this study, nanocrystalline ZnO doped with Bi (nc-ZnO:Bi) was synthesized by spin coating with sol-gel technique in order to form several ten nanometer film thicknesses. Dependent low-temperature effects on micro-nano-structural, optical and photocurrent properties of nc-ZnO:Bi films were investigated to validate the optimum condition. In order to accomplish in ETL function for emerging solar cell, annealing condition preparations of nc-ZnO:Bi films have been concerned at lower temperature than 600 °C. While the surface morphologies of ZnO nanostructures are largely adjustable by the growth conditions, they can be further formed differently by additive surfactant and annealing treatments. The optimized properties of nc-ZnO:Bi are closely relevant to the surface morphology features resulting in toward high solar cell efficiency.

The surface morphology was imaged by using field emission scanning electron microscope (Carl Zeiss series Auriga) (FESEM). The electrical property (J-V curve) under dark and illumination ($1.77 \text{ mW}/\text{cm}^2$) conditions was measured by using a Keithley (Series 2400 Electrometer) with 2-probe Ag contacts. The optical transmittance and reflectance were measured by UV-VIS spectrophotometer (Cary300) in mode integrating sphere with the range of 300-800 nm. Photosensitivity values of nc-ZnO:Bi films were calculated by using the experimental photocurrent under light intensity of $1.77 \text{ mW}/\text{cm}^2$. The film thickness was measured by optical profiler (Bruker).

2. MATERIALS AND METHODS

ZnO thin films doped with bismuth were prepared by spin coating technique. The precursor chemical of ZnO sol-gel consists of zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_{2,2} \text{H}_2\text{O}$) (CARLO) was used as ZnO source. Bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_{3,3.5} \text{H}_2\text{O}$) (Fluka) was used as a dopant source and the solvent of the gel consists of Ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) (CARLO) and ethanolamine ($\text{HOCH}_2\text{CH}_2\text{NH}_2$) (CARLO). The 0.7 M of zinc acetate was dissolved in solution of ethylene glycol-MEA and molar ratio of Zn:MEA was kept at 1:1. The mixture was stirred at 80 °C and then added bismuth nitrate pentahydrate of the concentration 0.2 at.%. The mixture was continuously stirred at 80 °C for 1 hour and then slowly dropped cetyltrimethylammoniumbromid (CTAB) as a surfactant which has been used for quality enhancement of the obtained ZnO:Bi films. With the concentration of 0.3 wt% in the gel solution, the mixture was continuously stirred at 80 °C for 30 min and then aged at room temperature for 24 hours. The processing steps are shown in the Figure 2.

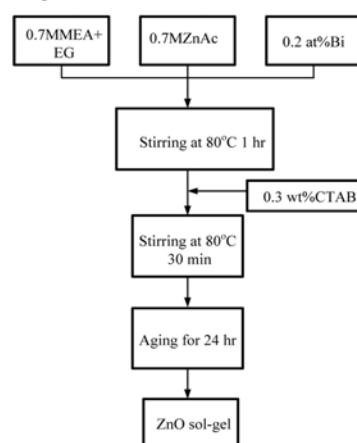


Figure 2. Schematic diagram of preparation Bi-doped ZnO sol-gel.

After aging the gel, the fused quartz substrates were carefully cleaned by Ratio Corporation of America (ARC) process and coated on the fused quartz substrates (size $24.5 \times 24.5 \text{ mm}^2$) by using a spin coater at 500 rpm for 15 sec. and at 3000 rpm for 40 sec., respectively. The thin films were dried at $250 \text{ }^\circ\text{C}$ for 30 minutes for 1 layer. ZnO:Bi multilayers were performed to obtain more film thickness with high quality of film. Optimal of film layers thus to lead to high properties were verified. Finally, the films were annealed at varying temperatures

between $350 \text{ }^\circ\text{C}$ and $550 \text{ }^\circ\text{C}$ in forming gas ambient for 2 hours.

3. RESULTS AND DISCUSSION

3.1 Surface Morphology

Nanocrystalline ZnO:Bi films prepared successfully by the sol-gel solution without using additive surfactant were presented in our previous work [12]. Even though Bi atoms incorporating in-phase with nc-ZnO showed the high crystallite quality, their surface qualities were not good enough for optoelectronic applications.

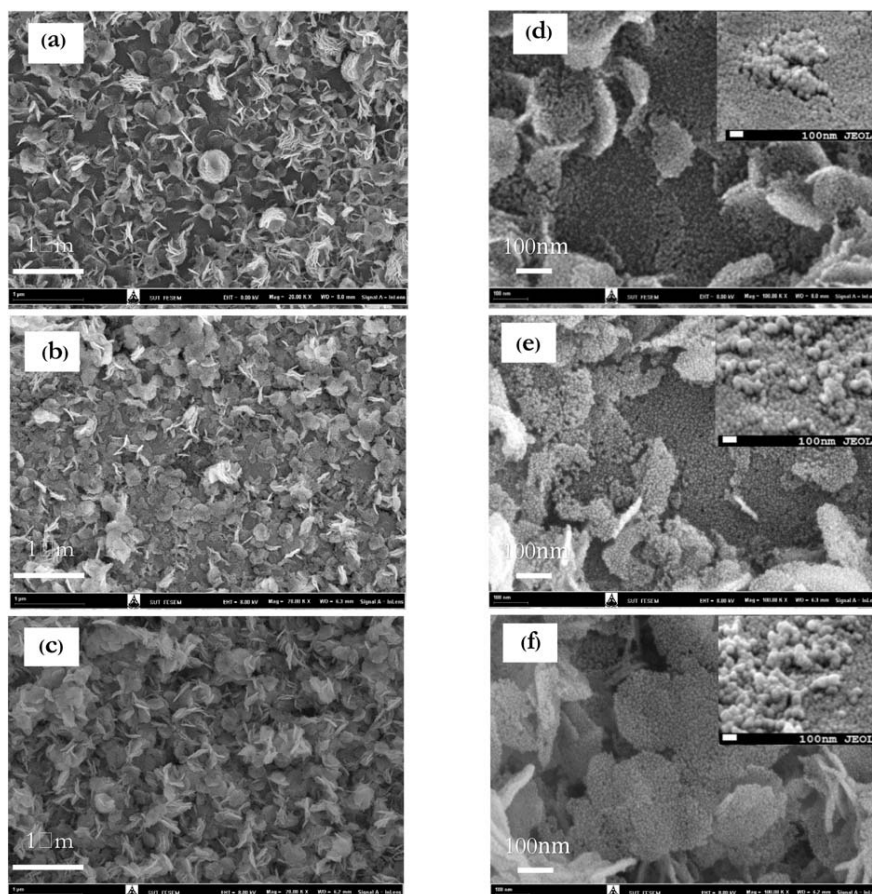


Figure 3. FESEM images in 20k and 100k magnifications of ZnO:Bi surface morphologies with coating layers at (a)(d) 4 layers, (b)(e) 5 layers, and (c)(f) 6 layers, respectively.

In this work, the sol-gel process and its solution thus have been developed with using suitable additive surfactant (CTAB).

Figure 3 (a), (b), and (c) shows the FESEM images (20k magnification) of ZnO:Bi films. which annealed at 550 °C with different repeat coatings at 4, 5, and 6 layers, respectively. It is found that pores and cracks are not appeared on surface of all film but distinctive petal-like surface morphologies are occurred. In Figure 3 (d), (e), and (f) with 100k magnification, higher density of spherical nanocrystalline ZnO:Bi particles (~10-20 nm diameter sizes as shown in the inset) are found when film coatings increase from 4 to 6 layers. More coatings are available to provide the increase in thickness of 118, 157, 202 nm, respectively. Roughness of surface morphology was found similarly with ZnO nanostructure produced by rf-sputtering technique [16]. Spherical ZnO nanoparticles with average diameter size of several ten nanometers were a formed by other preparation methods with using different dopants [17-18]. Spherical nc-ZnO:Bi morphology is the most promising to increase light-trapping potential, which will be leading to enhance solar cell quantum efficiency.

3.2 Transmittance and Reflectance Properties

Figure 4 shows the transmittance spectra in the wavelength range of 300-800 nm for nc-ZnO:Bi films composing of the different number of coating layers at temperatures preparation conditions. It is found that all films exhibit transmittance over than 80 % in wavelength range of 390-800 nm in range of 390-800 nm. In the UV range (300-380 nm) nc- ZnO:Bi films affects a steep decline in (< 20%) the transmittance spectrum as shown in Figure 4(a)-(b). Meanwhile, the larger

number of coatings affects a decrease in transmittance spectrum in the wavelength range between UV and blue light.

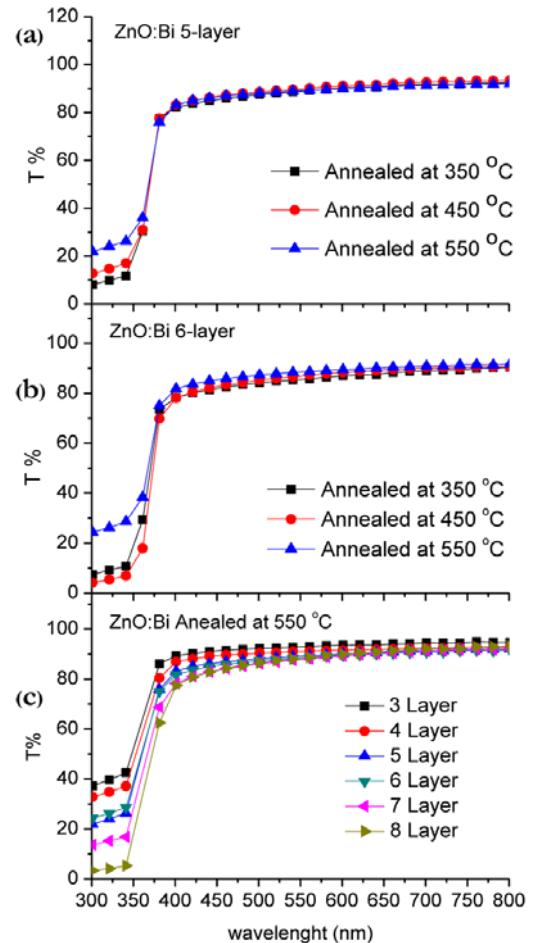


Figure 4. Transmittance spectra of nc-ZnO:Bi thin films with varying temperature conditions for (a) 5 layers (b) 6 layers and (c) varying coating layers.

Figure 5 presents the low effective reflectance that is less than 17% for all nc-ZnO:Bi films due to requirement of high light-absorption which is inversely proportional to reflectance. Low light-reflectance of film can provide the most promising light-trapping performance and reduce optical loss in solar cell approach. The 550 °C condition for preparing effective samples has no strong effect on the significant

increase of reflectance as shown in Figure 5 (a)-(b), while the larger number of coatings affects the increase of reflectance, considerably as observed in Figure 5 (c).

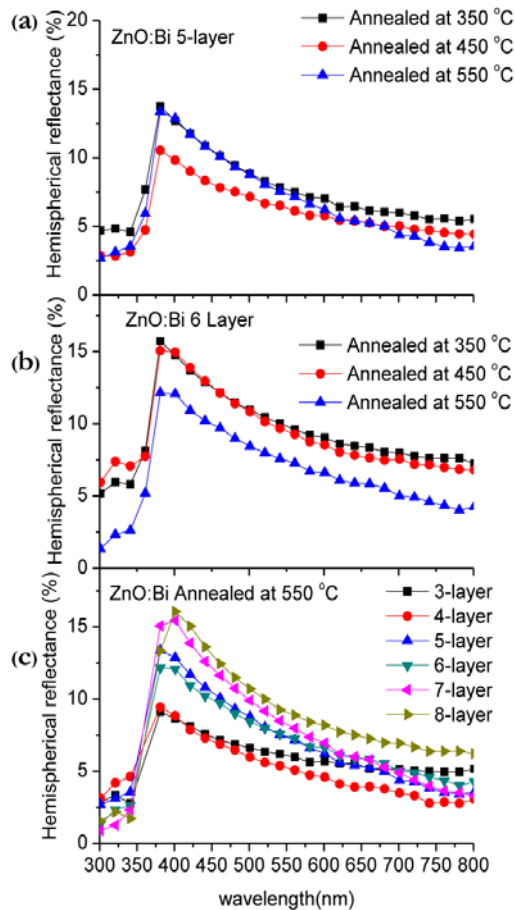


Figure 5. Reflectance spectra of nc-ZnO:Bi thin films with varying temperature conditions for (a) 5 layers (b) 6 layers and (c) varying coating layers.

3.3 Optical Band Gap

As a result of nc-ZnO:Bi behaving as a direct band gap semiconductor, photon light that is more than optical band gap (E_g) of nc-ZnO:Bi can produce electron-hole pairs without much momentum loss. Thus, E_g implies the minimum energy which can be absorbed in a semiconductor material and its carriers can be excited to become free carriers. E_g can be estimated by an extrapolation of

the linear curve portion as a function of absorption coefficient (5) depending on photon energy ($h\nu$) [19].

$$(\alpha h\nu)^2 = C(h\nu - E_g) \quad (1)$$

where C is a constant for a direct transition and photon energy.

The optical absorption coefficient of the prepared thin films can be calculated by [20].

$$\alpha = \frac{1}{t} \ln \left(\frac{\sqrt{(1-R)^4 + 4T^2R^2} - (1-R)^2}{2TR^2} \right) \quad (2)$$

where t is the thickness of the film, T and R are the transmittance and reflectance of the film, respectively.

Figure 6 (a)-(b) illustrates the plot of the relationship between $(\alpha h\nu)^2$ and $h\nu$ for nc-ZnO:Bi films with varying temperature conditions. It is noted that the estimated E_g of 5- and 6-layer nc-ZnO:Bi films slightly shifts at lower energy from 3.38 eV to 3.33 eV when they were annealed at higher temperature from 350 °C to 550 °C. The difference of E_g about 400-500meV with temperature dependence was observed in other reports [21-23]. The extension of E_g with decreasing temperature is most likely due to quantum size effect from smaller crystallite size as referred from study in the density functional theory [24].

In Figure 6(c), there is no change of E_g for nc-ZnO:Bi films composed of the different number of coating layers between 3 and 8 layer at 550 °C. It is revealed that the crystallinity become fully independent from the number of coating layers of the nc-ZnO:Bi. These results show the similarity with the previous research to prove by FESEM [25]. As a result of wide energy band gap, E_g , thus spherical nc-ZnO:Bi film is a high performance candidate for layer in solar cell.

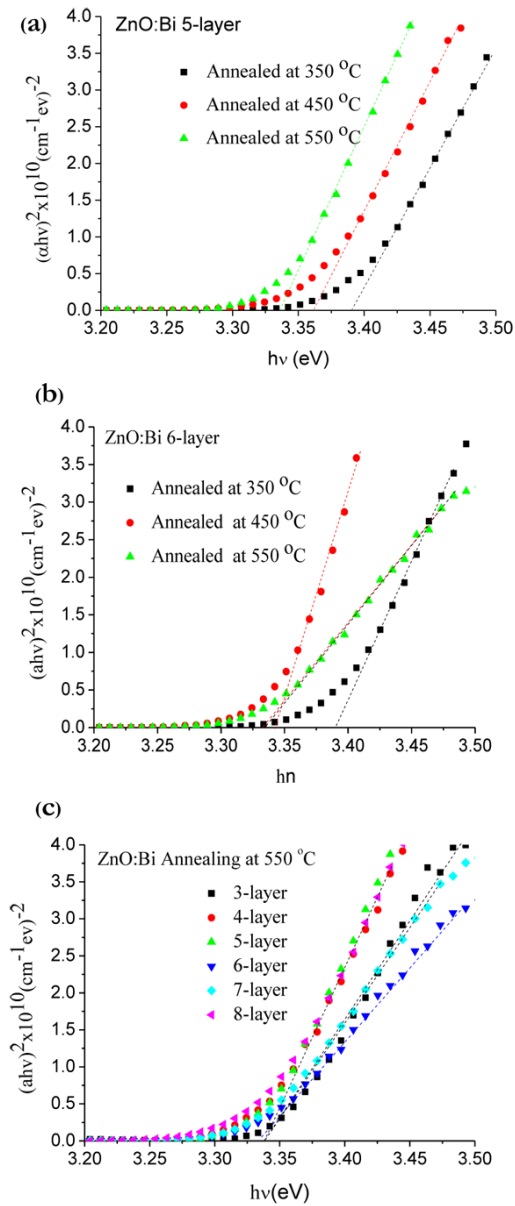


Figure 6. plot of $(\alpha hv)^2$ vs. $h\nu$ for nc-ZnO:Bi thin films with varying temperature conditions for (a) 5 layers (b) 6 layers and (c) varying coating layers.

3.4 Electrical Properties

Figure 7 presents J-V curve in semi-log scale of nc-ZnO:Bi films with varying number of coating layers and annealing temperatures under dark and illumination tests. It is significantly noted that the thin films with all

preparation conditions measured in illumination condition show the increasingly gain of photocurrent density comparing with dark current.

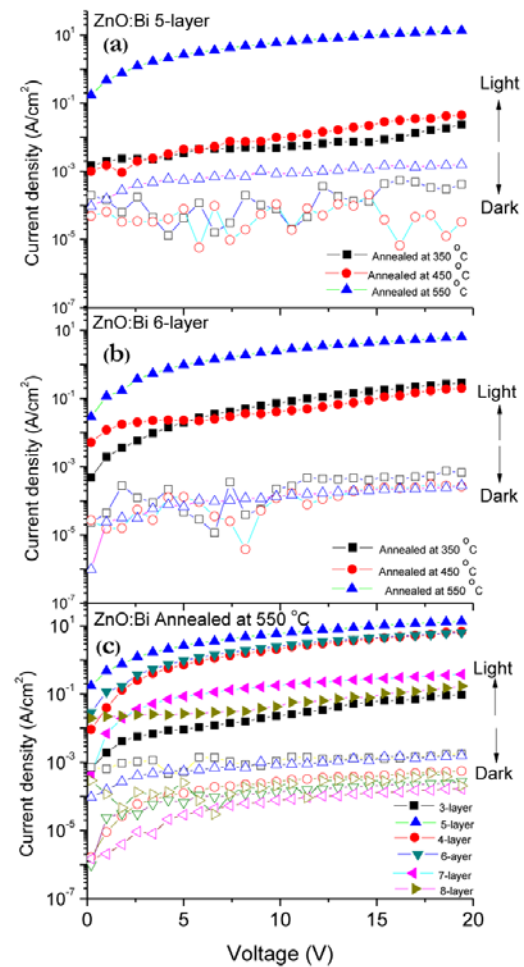


Figure 7. The plot of J-V curve in various annealing temperature and coating layers for nc-ZnO:Bi films with (a) 5-layer, (b) 6-layer and (c) layer dependence annealed at 550 °C.

As observed in Figure 7 (a)-(b) the nc-ZnO:Bi films annealed at 550 °C provide the maximum photocurrent whereas films prepared at low temperature (<500 °C) contribute less photocurrent. These results have agreement with previous work found less amount of ZnO:Bi crystallite [12]. The optimum number of nc-ZnO:Bi coatings

of 5-layer is able to provide the maximum photocurrent as shown in Figure 7 (c). It is mostly due to the existence of distinctive petal-like surface morphologies of nc-ZnO:Bi film with its appropriate spherical nanoparticles.

The photocurrent gain comparing with its dark current is presented in Figure 8 under the various coatings and annealing temperature conditions. In Figure 8 (a),

photocurrent gain increases with higher annealing temperatures. It is clearly found that a large number of photocurrent gain of nc-ZnO:Bi film is above 1×10^4 times for optimum 6-layer sample as illustrated in Figure 8 (b). Owing to roughness of spherical nc-ZnO:Bi surface, it is mostly available to result in further light-trapping performance and observed high photocurrent density.

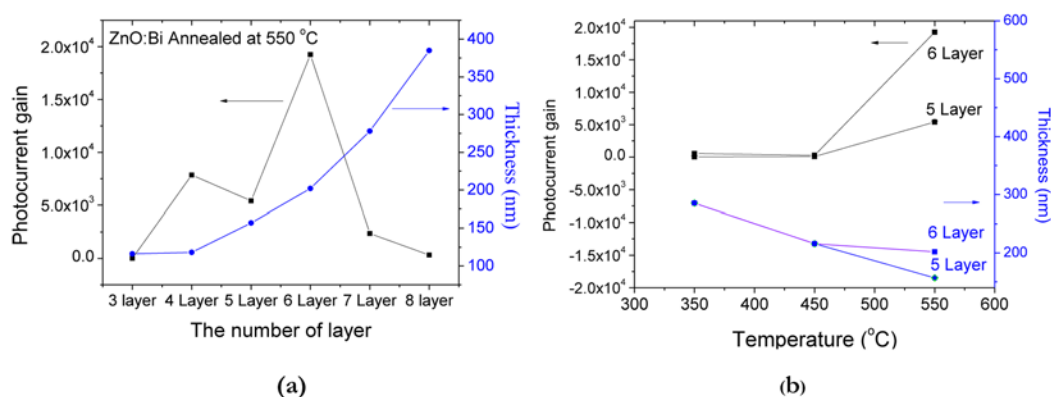


Figure 8. Photocurrent gain for nc-ZnO:Bi with (a) various anneal preparation conditions, coating layer dependence and (b) varying coating layers annealed at 550 °C.

Table 1. Comparison of current density of different metal oxide films with our nc-ZnO:Bi film.

Reference	J (mA/cm ²)	Preparation method	Material
Sasinska A. <i>et.al</i> [25]	9×10^{-1} (at 0.8 V)	Atomic layer deposition	TiO ₂
Randeniya L.K. <i>et.al</i> [26]	5.5×10^{-1} (at 0.8 V)	Plasma assisted chemical vapor deposition	TiO ₂
Hwang Y.J. <i>et.al</i> [27]	3×10^{-1} (at 0.5 V)	Atomic layer deposition	n-Si/n-TiO ₂
Mi Y. <i>et.al</i> [28]	9×10^{-1} (at 0.8 V)	Atomic layer deposition	AZO/TiO ₂ nanocone array
Chakraborty M. <i>et.al</i> [29]	2×10^{-1} (at 0.8V)	hydrothermal	ZnO nanorod
This work	3.98×10^2 (at 0.8V)	Sol-gel	nc-ZnO:Bi

High photosensitivity of nc-ZnO:Bi films (6 cm² area size) was obtained in the range of 8 -28 A/mW. Table 1 details the comparison of photocurrent density values of other metal oxide films and nc-ZnO:Bi film. At low applied voltage (0.5 and 0.8 V)

photocurrent density of nc-ZnO:Bi film is able to provide the highest value. Thus, the formation of densely spherical nc-ZnO:Bi at the film surface is able to enhance optoelectrical performance for perovskite solar cell and opto-sensor devices.

4. CONCLUSIONS

Spherical nanocrystalline ZnO:Bi films successfully coated on the fused quartz substrate have been prepared by sol-gel method. Distinctive petal-like surface morphology was occurred with in spherical nc-ZnO particles size of 10-20 nm. Optimal morphology roughness of 6-coating layer film annealed at 550 °C resulted in the less reflectance, photocurrent gain and photosensitivity performances which are able to contribute electron transport layer availability for perovskite solar cell. Moreover, wide energy band gap, E_g (3.33-3.38 eV) of nc-ZnO:Bi film indicates high responsibility of wide range of photon energy which is a good property for window layer of solar cell.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge Suranaree University of Technology, Thailand for financial supports and Synchrotron Light Research Institute of Thailand for providing technical research encouragement and measurements.

REFERENCES

- [1] Ko S.H., Park I., Pan H., Misra N. and Rogers M.S., *Appl. Phys. Lett.*, 2008; **92**: 154102-154103.
- [2] John F.W., Douglas A.K. and Rick E.P., *Transparent Electronics*, Springer US, Springer-Verlag US, 2008.
- [3] Sharma A., Franklin J.B., Singh B., Andersson G.G. and Lewis D.A., *Org. Elec.*, 2015; **24**: 131-136.
- [4] Akhavan O., Mehrabian M., Mirabbaszadeh K. and Azimirad R., *J. Phys. D: Appl. Phys.*, 2009; **42**: 225-305.
- [5] Huang J., Wu Y., Gu C., Zhai M., Sun Y. and Liu J., *Sens. Actuators B*, 2011; **155**: 126-133.
- [6] Kim H.S., Mora-Sero I., Gonzalez-Pedro V., Fabregat-Santiago F., Juarez-Perez E.J., Park N.G. and Bisquert J., *Nature Commun.*, 2013; **4**: 2242.
- [7] Son D.Y., Im J.H., Kim H.S. and Park N.G., *J. Phys. Chem. C*, 2014; **30**: 16567-16573.
- [8] Yang J., Siempelkamp B.D., Mosconi E., De Angelis F. and Kelly T.L., *Chem. Mater.*, 2015; **27**: 4229-4236.
- [9] Ana Q., Fassla P., Hofstettera Y. J., Becker-Kocha D., Bauscha A., Hopkinsona P.E. and Vaynzofa Y., *Nano Energy*, 2017; **39**: 400-408.
- [10] Lee M.M., Teuscher J., Miyasaka T., Murakami T.N. and Snaith H.J., *Science*, 2012; **338**: 643-647.
- [11] Jiang M., Liu X. and Wang H., *Surf. Coat. Technol.*, 2009; **203**: 3750-3753.
- [12] Krongarrom P., Rattanachan S.T. and Fangsuwannarak T., *Eng. J.*, 16, 2012; **3**: 59-70.
- [13] Kiomarsipour N. and Razavi R.S., *Superlattice. Microst.*, 2012; **52**: 704-710.
- [14] Kumar N.S., Bangera K.V. and Shivakumar G.K., *Superlattice. Microst.*, 2014; **75**: 303-310.
- [15] Muthukumaran S. and Gopalakrishnan R., *Opt. Mater.*, 2012; **34**: 1946-1953.
- [16] Ismail A. and Abdullah M.J., *J. King Saud Univ. Sci.*, 2013; **25**: 209-215.
- [17] Suliman A.E. and Tang Y., *J. Appl. Sci.*, 2007; **7**: 314-316.
- [18] El-Agez T.M., El Tayyan A.A., Al-kahlout A., Taya S.A. and Abde-Latif M.S., *Int. J. Mater. Chem.*, 2012; **2**: 105-110.
- [19] Pankove J.I., *Optical Processes in Semiconductors*, Dover Publications, New York, 1976.

- [20] Schroder D.K., *Semiconductor Material and Device Characterization*, Wiley, New York, 1990.
- [21] Xue S.W., Zu X.T., Zhou W.L., Deng H.X., Xiang X., Zhang L. and Deng H., *J. Alloys Compd.*, 2008; **448**: 21-26.
- [22] Cho S., *Trans Electr. Electron. Mater.*, 2009; **10**: 185
- [23] Krongarrom P., Rattanachan S.T. and Fangsuwannarak T., *ECTI Association of Thailand - Conference*, 2011; 50-53.
- [24] Schoenhalz A.L., Arantes J.T., Fazzio A. and Dalpian G.M., *J. Phys. Chem. C*, 2010; **114**: 18293-18297.
- [25] Sasinska A., Singh T., Wang S. and Mathur S., *J. Vac. Sci. Technol.*, 2015; **33**: 0734-2101.
- [26] Randeniya L.K., Bendavid A., Martin P.J. and Preston E.W.P., *J. Phys. Chem. C*, 2007; **111**: 18334-18340.
- [27] Hwang Y.J., Boukai A. and Yang P., *Nano Lett.*, 2009; **9**: 410-415.
- [28] Mi Y., Wen L., Xu R., Wang Z., Cao D., Fang Y. and Lei Y., *Adv. Energy Mater.*, 2016; **6**: 1501496-1501503.
- [29] Chakraborty M., Roy D., Biswas A., Thangavel R. and Udayabhanu G., *RSC Adv.*, 2016; **6**: 75063-75072.