ZnO wide bandgap semiconductors preparation for optoelectronic devices

A H Ramelan¹, S Wahyuningsih², H Munawaroh², R Narayan³
¹Electronic Materials and Energy Research Group, Faculty of Mathematics and Natural Sciences, Sebelas Maret University, Jl. Ir. Sutami No. 36A Surakarta, INDONESIA
²Inorganic Materials Research Group, Faculty of Mathematics and Natural Sciences, Sebelas Maret University, Jl. Ir. Sutami No. 36A Surakarta, INDONESIA
³Biomedical Engineering Joint Department of University of North Carolina/North Carolina State University, USA

E-mail: aramelan@mipa.uns.ac.id

Abstract. ZnO nanoparticles were successfully synthesized by sol-gel method. According to unique structural and optical properties of ZnO semiconductor material, there are many potential important applications based on that material, including as an anti-reflection coating (ARC) in solar cells. Antireflective coatings (ARC) made of ZnO on top to improve the optical properties of the coating. TiO₂ layer have been coated on a ZnO nanoparticle layer. ZnO nanoparticle was characterized by X-ray diffraction (XRD), Scanning electron Microscopy (SEM) and UV-Vis spectroscopy. ZnO annealed at a temperature of 600 °C have the greatest crystalinity and crystal size than that at a temperature of 400 °C and 500 °C. SEM images of ZnO shown agglomeration and grain size increases with increasing annealed temperature. While, the optical properties of ZnO increase with increasing annealed temperature. The optical transmittance spectra of the ZnO are shown that the increasing annealing temperature had effectively improved the optical transmittance of the films. While, reflectance (%R) properties shows that, the higher annealing temperature of ZnO preparations can decrease of %R value of ZnO thin layer. The difference properties of ZnO are due to differences of light scattering resulting from the crystal size effect. The ZnO prepared by annealed at 600 °C gain a good performance of the lowest reflectance value and highest size crystal. By the addition of ARC ZnO 600 °C we have been capable improve cell performance so that that cells achieve an efficiency of 0.27%.

1. INTRODUCTION

Zinc oxide, ZnO, is a direct wide bandgap semiconductor. Many of its properties promise for many optoelectronic device applications. One of these applications is dye sensitized solar cells (DSSC). DSSC is an attractive alternative to photovoltaic development as compared to conventional photovoltaic device (silicon solar cells) due to low prices and simple fabrication [1]. However, the efficiency of DSSC is still low than silicon solar cells. One way to increase the efficiency of DSSC is use a material that acts as an anti-reflection coating (ARC). ZnO is attractive as an ARC material because of its good transparency in the visible range and high absorption in the UV range because the wide band gap energy of ZnO monocrystal which is 3.1-3.3 eV at room temperature, and 3.44 eV at a temperature of 4 K. Meanwhile, as polycrystalline ZnO films is between 3.28 to 3.30 eV [2]. It's
assisted in electron transfer from valence band to conduction band and increase light harvesting of DSSC [3].

ARC made of ZnO on top of layer will capable to improve the optical properties of the coating. A thickness of 30 nm has been considered for the ITO layer in the case of a hybrid coating. Reducing the ITO thickness down to 30 nm, compared to a more standard value around 50-70 nm, yields a lower useless absorption in the TCO layer. This reduction is made possible in the case of our hybrid design, since the top ZnO layer will also contribute to the lateral conduction of electrical charges. Great crystal size has a great internal trajectory, where the photon absorption takes place following the Lambert-Beer law. At the relatively smaller size, there are proportionately more than the surface reflection of internal photon path length, so it will be higher reflectance [4].

Synthesis of ZnO by deposition techniques such as electrodeposition [5], co-precipitation [6], hydrothermal [7], and sol–gel process [8]. Among the different deposition techniques, sol–gel process possess several distinct process advantages such as large area capability, glass compatible process, low-cost set-up and precise control of the film composition. Physical properties of sol–gel deposited thin films are strongly influence by pH of the initial precursor [9], dopant concentration [10], calcination temperature [11], solvent selection [12].

This study reports on the synthesis and characterization of ZnO by sol–gel technique. The aim of this work is to evaluate the microstructure properties of ZnO as a function of calcination temperature and evaluation of optoelectronic DSSC.

2. EXPERIMENTAL

2.1 Synthesis of ZnO nanoparticle

ZnO samples were prepared by a simple sol-gel method. 0.5 M of zinc acetate dehydrate (Zn(CH₃COO)₂·2H₂O, Aldrich) was dissolved in 30 mL of ethanol. Then, 30 mL of Polyethylene Glycol 1000 (PEG) 0.5 M was add into these solution. The solution was stirred at 60 °C for 2 hour till gel formation. After that, the solutions were placed in an oven at 60 °C until the solvent evaporated. Finally, ZnO were annealed at a temperature of 400 °C, 500 °C, and 600 °C. Final product are nanoparticles of ZnO. Structural and optical properties of synthesized ZnO was conducted by XRD, SEM and spectroscopy Uv-Visible.

2.2 Fabrication of DSSC

DSSC fabrication used ITO glass as a substrate. ZnO nanoparticle about 0.1 grams was dissolved in 2 mL of ethanol to obtain a paste. The paste was then coated on ITO glass with slip coating method. ITO was coated of ZnO heated at a temperature of 300 °C for 30 minutes. Then, ITO was coated TiO₂ paste. Pt paste was also superimposed on another ITO glass to built counter electrode thin film. Both ITO based electrode was heated at a temperature of 300 °C for 30 minutes. Photo anode TiO₂ with anti-reflecting ZnO was soaked in a dye solution of N3 ruthenium complexes for 24 hours. Then, both electrodes were sealed and given a distance to immerse the electrolyte solution. The electrolyte was prepared from potassium iodide (KI) of 0.4 grams and iodine (I₂) of 0.0635 grams dissolved in 5 mL acetonitrile. After the electrolyte was immersed, the DSSC were characterized by an I–V Keithley 2602A measurement.

3. RESULT AND DISCUSSION

3.1 Structure of ZnO

ZnO was synthesized using precursor Zn(CH₃COO)₂·2H₂O by the simple sol-gel method. Preparation of ZnO were using polyethylene glycol as a surfactant. The solution was stirred at 60 °C for 2 hour till gel formation. The solution were dried at 60 °C following by annealing process at a temperature of 400 °C, 500 °C and 600 °C, and then it was characterized by XRD. The characterization results of XRD were shown in Fig. 1, which shows that the crystalline structure in accordance with the wurtzite hexagonal structure (JCPDS 80-0075) with dominant peak at 2θ = 31.6; 34.4; 36.2. In Fig. 1, it can be seen that the particles formed is ZnO and crystallinity of particle increase with increase annealing
temperature. At high temperature, 600 °C, peak of ZnO seem sharp and clearly, the particles have a high crystallinity was explained by sharp peak and the highest intensity than crystallinity at lower temperature. This is due to the higher temperature affect evaporation process and inter particle reaction more perfect, so can increase of crystalline formation. In addition, increase of annealing temperature can increases the reaction rate of decomposition of precursors [13].

![X-ray diffraction pattern of ZnO annealed at 400 °C, 500 °C, and 600 °C](image)

**Figure 1.** X-ray diffraction pattern of ZnO annealed at 400 °C, 500 °C, and 600 °C

Temperature dependence of ZnO nanoparticle crystal growth was shown in Table 1. ZnO annealed at a temperature of 600 °C have greatest crystal size than that at temperature of 400 °C and 500 °C. This is because of the higher temperature, the faster particle nucleation rate. It was also been produced by Ivanova et al. (2010) [14] and Gondal et al. (2009) [15], meanwhile increase of annealing temperature can increases crystal size. It may because the higher the calcination temperature the rate of nucleation and growth of material more quickly so that more perfect crystal growth.

| Annealed Temperature (°C) | λ (nm) | B (deg) | (rad) | 2θ (deg) | Cos θ | D (nm) |
|---------------------------|-------|---------|------|--------|------|------|
| 400                       | 0.154 | 0.403   | 0.007| 36.407 | 0.949| 20.750|
| 500                       | 0.154 | 0.317   | 0.005| 36.147 | 0.950| 26.374|
| 600                       | 0.154 | 0.290   | 0.005| 34.660 | 0.954| 28.651|

The study morphology of ZnO were investigated using Scanning Electron Microscopy and shown in Fig. 2. It was seem that agglomeration and grain size increases with increasing annealed temperature. This is because annealed temperature affect of grain growth ZnO [16].

![SEM image of ZnO](image)

**Figure 2.** SEM image of ZnO (a) 400 °C, (b) 500 °C, and (c) 600 °C
3.2 Optical Properties of ZnO

Optical properties of ZnO material is characterized by a UV-VIS spectrophotometer. The analysis was performed in the wavelength range from 200 nm to 800 nm, the data obtained from this analysis is the absorbance and wavelengths are shown in Fig. 3. It can be seen that ZnO synthesized at higher annealing temperature capable increase the light absorption. The maximum wavelength absorption of ZnO is at 342 nm.

![Figure 3. Absorption spectra’s of ZnO](image)

The optical transmittance spectra of the ZnO are shown in Fig. 4. In Fig. 4 shown that the increasing annealing temperature have effectively improved the optical transmittance of the films. The annealing temperature of 400 °C, 500 °C, and 600 °C have produced ZnO with average optical transmittance of 58%, 61%, and 68%, respectively. The improved optical transmittance is due to the better formed crystallite with the increase of annealing temperature.

![Figure 4. Transmittance spectra’s of ZnO annealed at 400 °C, 500 °C, and 600 °C.](image)

Reflectance (%R) properties show that the higher annealing temperature of ZnO preparations cause decrease of %R value of ZnO thin layer (Fig. 5). ZnO annealed at 400 °C was gained %R = 60.54%, at 500 °C was gained %R = 49.56% and at 600 °C was gained %R = 30.12%. The difference properties are due to differences of light scattering resulting from the crystal size effect.
The optical band gap was determined using Tauc method [17]. The optical band gap was measured as an indirect band semiconductor. The value of the optical band gap is obtained by linearly extrapolating the linear portion to $y = 0$. Fig. 6 shows the function of $(\alpha h \nu)^2$ vs photon energy for ZnO with different annealing temperatures. The estimated optical band gap of ZnO at temperature 400 °C, 500 °C, and 600 °C was 3.36 eV, 3.35 eV and 3.38 eV, respectively. These values were very close to the band gap of intrinsic ZnO which is 3.37 eV [18]. The reduction of the optical band gap with increasing annealing temperature can be due to the improved crystallinity and decreased defects of the films with higher annealing temperature. Similar results have been reported in the work of Jianguo et al. [19] and Mudjat et al. [20].

Figure 6. The optical band gap of ZnO

3.3 Fabrication of DSSC
DSSC performance conducted on TiO$_2$ that modified with anti-reflection ZnO layer. At this DSSC experiment, we use N3 dye as a standard dye. DSSC performance testing has been carried out with equipment Keithley IV meter with $P = 1000$ W/m$^2$. It was concluded that the ZnO prepared by
annealed at 600 °C gain a good performance of the lowest reflectance value and high transparency. The maximum performance of DSSC if we use the photoanode TiO$_2$ at coated anti-reflection ZnO with annealing temperature of 600 °C. Fig. 5 shows the I-V curve result of DSSC performance by the addition of anti-reflection ZnO we have been capable improve cell performance so that cells achieve an efficiency of 0.27%.

![Image of I-V characteristic](image)

**Figure 7.** I-V characteristic of DSSC build by ZnO-coated TiO$_2$ at dark condition (black line) and under illumination condition (red line).

4. CONCLUSION
ZnO nanoparticle were synthesized by sol-gel method. The structural and optical properties of ZnO nanoparticle have been investigated. Annealed temperature influence the crystalline quality of ZnO, where increasing of annealing temperature was followed by increase of crystallinity and crystal size of ZnO. SEM images of ZnO shown agglomeration and grain size increases with increasing annealed temperature. And optical properties of ZnO increase with increasing annealed temperature. Increased optical properties of ZnO can improve efficiency of DSSC. The increase of annealed temperature can increase of optical transmittance spectra and decrease of %R value of ZnO thin layer. The ZnO prepared by annealed at 600 °C gain a good performance of the lowest reflectance value and highest size crystal. By the addition of ARC ZnO 600 °C we have been capable improve cell performance so that that cells achieve an efficiency of 0.27%.

ACKNOWLEDGMENT
The authors would like to acknowledge the International Research Collaboration and Scientific Publications Program, Ministry of Research, Technology and Higher Education, Republic of Indonesia, for supporting this research and to the Integrated Mathematics and Natural Science Laboratory of Sebelas Maret University for supporting and providing the facilities for this research.

REFERENCE
[1] Gratzel M 2003 *Photochemistry Reviews* 4 145–153.
[2] Dengyuan Song 2005 *Tesis Doktor at University of New South Wales*.
[3] Lee, S Chang, Y L, Li-Ying H and Jung-Fu 2011 *Journal Engineering Technology and Education* 5 545-552.
[4] Boden S A and Bagnall D M 2006 *Proc. of 4th world conference on photovoltaic energy conversion IEEE* (1-424400016-3) 1358-136.
[5] Salman KA, Omar K, and Hassan Z 2012 *Solar Energy* 86 541–547.
[6] P K Sharma, R K Dutta, and A C Pandey 2007 *J. Colloid Interface Sci* 345 149–153.
[7] Y Zhang, S Li, G Goh, and S Tripathy 2008 *Appl. Phys. Lett.* 93 10251.
[8] C Knies, M T Elm, P J Klar, J Stehr, D M Hofmannn and N Romanov 2009 J.Appl. Phys. 105 073918-7.
[9] L Spanhel and M A Anderson 1991 J. Am. Chem. Soc. 113 2826–2833.
[10] W Tang and D Cameron 1994 Thin Solid Films 238 83–87.
[11] K Kanade, B Kale, R Aiyer and B Das 2006 Mater. Res. Bull 41 590–600.
[12] M Ohyama, H Kozuka and T Yoko 1998 J. Am. Ceram. Soc. 81 1622–1632.
[13] Hidayat D, Ogi T, Iskandar F and Okuyama K 2008 Materials Sciences and Engineering B. 151 231-237.
[14] Ivanova T, Harizanova A, Koutzarova T and Vertruyen B 2010 Materials Letters 64 1147-1149.
[15] Gondal M A, Drmosh Q A, Yamani, Z H and Saleh, T A 2009 Applied Surface Science 256 298-304.
[16] Zi-Neng Ng and Kah-Yoong Chan 2012 Applied Surface Science 258(24) 9604–9609.
[17] J Tauc, R Grigorovici and A Vancu 1966 Physics Status Solid B 15 (2) 627–637.
[18] X Zhao, J Y Lee, C R Kim, J H Heo, C M Shin, J Y Leem, H Ryu, J H Chang, H C Lee, W G Jung, C S Son, B C Shin, W J Lee, S T Tan, J Zhao, X Sun 2009 Physica E 41 1423.
[19] J Lv, W Gong, K Huang, J Zhu, F Meng, X Song and Z Sun 2011 Superlattices and Microstructures 50 98–106.
[20] M Caglar, Y Caglar, S Aksoy and S Illican 2010 Applied Surface Science 256 4966–4971.