Highly oriented-ZnO nanorods from hydrothermally depositions: Synthesis and optical properties

R Kurniawan1,2,* , T E Setyawant1, W P Agista1, S Amalia1, Z A Pangestu1, N E A Wahyuni1, N S Febrianti1, and M H Habani1

1 Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang, Jl. Semarang 5, Malang 65145, East Java, Indonesia
2 Centre of Advanced Materials for Renewable Energy, Universitas Negeri Malang, Jl. Semarang 5, Malang, 65145, East Java, Indonesia

*Corresponding author: robi.kurniawan.fmipa@um.ac.id

Abstract. A highly (002)-oriented ZnO NRs on the Si/SiO$_2$ substrate was successfully synthesized by the spray-hydrothermal method, where ZnO nanoparticles (ZnO NPs) were used as templates. Interestingly, by varying deposition temperatures from 150 to 350 °C, we successfully modified the orientation of the nanorod from vertical/horizontal to globular. This result is related to the agglomeration of ZnO NPs in the deposition process. Furthermore, globular ZnO NR showed a high electron transfer up to $\sim 9 \times 10^{14} \Omega^{-1} \text{cm}^{-1} \text{eV}$ with the presence of an excitonic state. Our results will provide an alternative in designing the structure and morphology of ZnO NR at a more affordable cost for high-performance optoelectronic applications.

1. Introduction

Zinc oxide (ZnO) is one of the wide band gap semiconductors that is widely used in nanotechnology because of its superior characteristics. Among several type morphologies, 1-D ZnO, such as ZnO nanorods (ZnO NRs) and ZnO nanowires (ZnO NWs), attracts a lot of attention because it has a high surface-to-volume ratio. To control the morphology and structure of 1-D ZnO, it is generally carried out during the growing process. For example, to get a well-oriented ZnO NR done using a gas-phase deposition technique such as sputtering [1], which requires high temperature, high vacuum, and high cost [2]. Other techniques can also be used to produce highly-oriented ZnO NR, for example using a template [3,4] and seeding [5–7], but that depends on the structural quality and morphology of the grown seed. Here, the liquid-phase deposition technique is cheaper than the gas-phase deposition technique, however, it provides limited control and results in lower sample quality compared to the gas-phase deposition technique.

Vertically (002)-oriented ZnO NR has been successfully obtained using seeds prepared with sol-gel spin coating and thermal annealing at 350 °C [8]. Other seed deposition methods have also been used to produce ZnO NR. The ZnO seed prepared with chemical vapor deposition (CVD) [9] and RF sputtering [10] was successfully used to produce (002)-oriented ZnO NR with a denser arrangement, where post thermal annealing plays an important role in controlling the diameter and size particle. Also, ZnO NR with other arrangements shows superior characteristics. ZnO NR 1-D and 3-D combinations such as urchin-like/globular were synthesized using plasma-enhanced chemical vapor deposition, which is very promising in improving performance for solar cell devices, lasers, piezo-nanogenerators [11].
urchin-like ZnO NR has high mechanical and chemical stability which is very potential in the development of pseudocapacitors [12]. The urchin-like ZnO NR deposited with atomic layer deposition has an ideal efficiency because it has a high surface area and specific porosity and good light trapping [13]. From the reports above, urchin-like / globular ZnO NR has advantages for various applications, however, it requires high tech sophisticated equipment and produces crystal orientation in 3 planes, (100), (002), and (101).

In this study, we synthesize the highly-oriented ZnO NR hydrothermally using ZnO NPs as a template. Here, the orientation of the ZnO NR was controlled by modifying the agglomeration of the ZnO NP. The investigation was focused on morphology, crystal structure, and optical properties of the ZnO NR. Our method would give an alternative for the synthesis of ZnO NR with the low-cost production.

2. Methods
Zinc oxide nanorods (ZnO NRs) grown on Si/SiO$_2$ substrate using the ZnO NPs template. The ZnO NPs were deposited using the spray method for 1 minute at a distance of 5 cm using the precursors of the Zn(CH$_3$COO)$_2$.2H$_2$O solution, which is explained elsewhere [14]. The deposition was performed by using a nozzle diameter of ~300 nm and different deposition temperatures of 150 °C, 250 °C, and 350 °C. Furthermore, the ZnO NR samples were prepared by the hydrothermal method using a precursor from the Zn(NO$_3$)$_2$.4H$_2$O solution prepared using the same procedure as the previous report [14]. Here, the samples were characterized using scanning electron microscopy (SEM) [type: FEI: INSPECT S50], X-ray diffraction (XRD) [type: PANalytical X'Pert Pro] and Spectroscopic Ellipsometry (SE) [type: Micropack: Spec-El 2000]. The crystal structure was analyzed using the Williamson-Hall plot [15] and the particle size was estimated by calculating the particle diameter distribution. The optical properties of the samples were studied by investigating the ratio of the amplitude reflection coefficients for p- and s-polarizations and spectral weight (SW) [16]. Furthermore, second derivatives were used to determine the critical point in the SW.

3. Results and Discussion
Figure 1 shows the surface morphology of ZnO nanoparticles deposited for 1 minute with different deposition temperatures, 150 °C (T-150), 250 °C (T-250), and 350 °C (T-350). The particle distribution calculation showed that the samples have a particle size of T-150, T-250, and T-350 have particle size distributions of 109 nm, 97 nm, and 62 nm. Here, the increase in deposition temperature significantly decreases particle size accompanied by the increase in particle agglomeration. Temperature and deposition time are important parameters in material growth during deposition, where temperature acts as an energy source in the nucleation and crystal growth. A specific temperature treatment will create competition between densification and coarsening which plays a role in the formation of pores (density) of the material on the substrate [17]. Our result showed that the agglomeration was accompanied by a dense particle (low porosity) with clear grain boundaries observed. As is well known, pores are a source of surface defects that promote a decrease in morphological properties [18,19]. The presence of small pores in our sample indicates that morphological defects can be minimized. Also, clear grain boundaries will act as a starting point for nanorod growth and allow nanorods to grow individually without any surface fusion.

Figure 2 presents the morphology of the ZnO NR grown by the hydrothermal method. It can be shown that with the same hydrothermal process, each sample has a different nanorod orientation. The ZnO NR T-150 sample has a random orientation, the ZnO NR T-250 sample has a more organized, forming vertical orientation in the middle and horizontal edges, and the ZnO NR T-350 sample has a globular orientation, as illustrated as in Figure 3. This difference in orientation is presumably due to the arrangement and distribution of ZnO NPs. The ZnO NR formation begins with nucleation and continues with crystal growth, here ZnO NP acts as a seed and becomes a starting point for growth for ZnO NR. Therefore, ZnO NP also acts as a template, where the growth of ZnO NR follows the arrangement and orientation of ZnO NP.
Figure 1. Morphology of the ZnO seed grown on Si/SiO₂ substrate with different deposition temperature; 150 °C (T-150), 250 °C (T-250) and 350 °C (T-350).

Figure 2. Morphology of the ZnO NR prepared by using ZnO seed with different deposition temperature; 150 °C (T-150), 250 °C (T-250), and 350 °C (T-350).

Figure 3. Schematic illustration of the ZnO NR prepared by using ZnO seed with different deposition temperature; 150 °C (T-150), 250 °C (T-250), and 350 °C (T-350).
Figure 4. Diffraction pattern (a) and W-H plot (b) of the ZnO NR prepared by using ZnO seed with different deposition temperature; 150 °C (T-150), 250 °C (T-250), and 350 °C (T-350).

Figure 5. Diffraction pattern (a) and W-H plot (b) of the ZnO NR prepared by using ZnO seed with different deposition temperature; 150 °C (T-150), 250 °C (T-250), and 350 °C (T-350).

As explained above, an increase in deposition temperature promotes morphological differences in ZnO NR. Figure 4 (a) shows the ZnO NR diffraction pattern on a Si/SiO$_2$ substrate with inset showing the ZnO NP diffraction pattern. The ZnO NR with the hydrothermal method generally has three diffraction peaks in fields (100), (002), and (101) [20–23]. We confirmed that all of our NR ZnO samples have a dominant crystal orientation in the plane (002). Here, an increase in peak intensity was observed at ZnO NR T-150 to T-350 without being accompanied by a shift in peak position. This orientation and increase in the intensity of ZnO NR are thought to be strongly related to the increase in deposition temperature [24] and the plane orientation of the ZnO NP, which acts as a template. Furthermore, the ZnO NR crystal structure was investigated by using the Williamson-Hall (W-H) plot. In the W-H plot analysis, the crystal properties were determined through the characteristics of full width at half maximum (FWHM). The width of the peak contributes to the size of the crystal and lattice strain, where the total FWHM is formulated by Equation (1) [15].
\[ B_{\text{total}} = B_{\text{size}} + B_{\text{strain}} \]  

(1)

with

\[ B_{\text{size}} = \frac{k\lambda}{D\cos\theta} \]  

(2)

and

\[ B_{\text{strain}} = \varepsilon \tan\theta \]  

(3)

By combining Equations (2) and (3), the \( B_{\text{total}} \) is obtained

\[ B_{\text{total}} = B = \frac{k\lambda}{D\cos\theta} + \varepsilon \tan\theta \]  

(4)

or can be rearranged into

\[ \frac{B\cos\theta}{\lambda} = \frac{k}{D} + \frac{\varepsilon \sin\theta}{\lambda} \]  

(5)

where \( B \) is FWHM, \( \theta \) is the diffraction angle (in °), \( \lambda \) is the X-ray wavelength (1.5406Å), \( k \) is a constant (~ 0.9), \( D \) is the crystalline size, and \( \varepsilon \) is the lattice strain. Figure 4 (b) shows the W-H plot for the ZnO NR samples. Based on the linear fitting, crystalline size and lattice strain were obtained, with crystalline size/lattice strains of 8.1Å/0.38, 11.7Å/0.99, and 4.4Å/0.74 for ZnO NR T-150, T-250, and T-350, respectively.

Figure 5 (a) shows the ratio of the amplitude reflection coefficients for p- and s-polarizations or rho (\( \rho \)). It can be seen that all samples have the same \( \rho \) pattern. Here, \( \rho \) shows the relationship between the amplitude ratio (\( \Psi \)) and the phase difference (\( \Delta \)) between p- and s-polarizations [16], which are formulated in Equation (6).

\[ \rho(N, d, \theta_0) \equiv \tan\Psi \exp(i\Delta) \equiv \frac{r_p}{r_s} \]  

(6)

where \( N \) is the complex refractive index that can be obtained from the fitting results, \( d \) is the thickness of the sample, \( \theta_0 \) is the angle of incidence, \( r_p \) and \( r_s \) are the amplitude of reflection for p- and s-polarizations. Furthermore, the electronic transfer of the sample was investigated by using the refractive index spectra. The complex refractive index is related to the dielectric function, which provides information on polarization and optical absorption of the sample. The relationship between the refractive index and the dielectric function is shown by Equation (7-10).

\[ N \equiv n - ik \]  

(7)

with

\[ N^2 \equiv \varepsilon \equiv \varepsilon_1 - i\varepsilon_2 \]  

(8)

where

\[ \varepsilon_1 = n^2 - k^2 \]  

(9)

and

\[ \varepsilon_2 = 2nk \]  

(10)

where \( n \) and \( k \) are the real and imaginary parts of the refractive index, \( \varepsilon_1 \) and \( \varepsilon_2 \) are the real and imaginary parts of the dielectric function. By using the value of the \( \varepsilon_2 \), we can then determine the electronic transfer through the spectral weight (SW) value. Here, the value of SW can be determined from the integral of optical conductivity (\( \sigma_1 \)), as formulated in Equations (11) and (12)

\[ \sigma_1(\omega) = \frac{\varepsilon_2(\omega)}{4\pi} \]  

(11)

with

\[ SW = \int \sigma_1(\omega)d\omega \]  

(12)
where $\omega$ is the angular frequency. Figure 5 (b) shows the spectral weight (SW) of the sample. As previously reported, ZnO has a band gap of $\sim 3.3$ eV [14]. The SW value shows the number of electron transfer from the valence band (VB) to the excitation states/conduction band (CB). The SW values in the range 2.0 - 3.3 eV indicate the presence of electron transfer. We suspect that the electron transfer at this range originates from the presence of defects in the system [25], however, to ensure this further characterization is needed. The results showed that the ZnO NR T-350 sample had the highest SW than that of the other samples. This result is presumably due to the distribution of material on the substrate and the high crystallinity of ZnO T-350, as explained in the SEM and XRD results above. The inset presents the second derivative SW of the samples, which provide a critical point of SW. All of the samples have a band gap ($E_g$) of 3.19 eV. Also, a critical point of 3.04 eV was observed in the ZnO NR T-350, which indicated an excitonic state ($E_{\text{ex}}$). The presence of an excitonic state We suspect that the presence of an excitonic state is strongly related to the high crystallinity of the ZnO NR T-350. Here, controlled morphology and high orientation of the ZnO NR will benefit us in designing this material for various optoelectronic applications, such as high-performance sensors/photodetectors and solar cells.

4. Conclusion
Highly-oriented ZnO NR has been successfully synthesized by spray-hydrothermal using ZnO NPs as a template. Deposition temperature provides favorable conditions for ZnO NP to conduct crystal growth with high orientation in the plane (002). The increase in deposition temperature promotes the increase in the distribution of ZnO NP with a decrease in grain size accompanied by an increase in agglomeration. The degree of agglomeration and arrangement of ZnO NP plays the important role in determining the orientation of the ZnO NR, with T-150 has the random nanorod orientation, T-250 has the vertical and horizontal nanorod orientation, and T-350 has the globular nanorod orientation. Furthermore, the ZnO NR T-350 sample shows the high electronic transfer up to $\sim 9 \times 10^{14} \text{ cm}^{-1} \text{eV}$ with the presence of an excitonic state due to high crystallinity. The results of this study can be used as a basis for developing high-performance devices based on ZnO NR for optoelectronic applications.

References
[1] Hieu H N, Vuong N M, Jung H, Jung D M, Kim D, Kim H and Hong S-K 2012 Optimization of a zinc oxide urchin-like structure for high-performance gas sensing J. Mater. Chem. 22 1127–34
[2] Mahmood M A, Jan S, Shah I A and Khan I 2016 Growth Parameters for Films of Hydrothermally Synthesized One-Dimensional Nanocrystals of Zinc Oxide International Journal of Photoenergy 2016 1–12
[3] Lai M and Riley D J 2006 Templated Electrosynthesis of Zinc Oxide Nanorods Chem. Mater. 18 2233–7
[4] Athauda T J and Ozer R R 2013 Nylon Fibers as Template for the Controlled Growth of Highly Oriented Single Crystalline ZnO Nanowires Crystal Growth & Design 13 2680–6
[5] Zhou F-C, Yuan L, Feng S-H, McLachlan M A and Zhang J-Q 2018 Seed-layer effect on highly oriented ZnO nanorod array fabrication Chinese Journal of Inorganic Chemistry 34 1655–62
[6] Wu W, Hu G, Cui S, Zhou Y and Wu H 2008 Epitaxy of Vertical ZnO Nanorod Arrays on Highly (001)-Oriented ZnO Seed Monolayer by a Hydrothermal Route Crystal Growth & Design 8 4014–20
[7] Toe M Z, Jusoh N A H N, Pung S Y, Yaacob K A, Matsuda A, Tan W K and Han S S 2019 Effect of ZnO Seed Layer on the Growth of ZnO Nanorods on Silicon Substrate Materials Today: Proceedings 17 553–9
[8] Xia Y M, Zhang Y F, Yu X Q and Chen F 2015 Controllable Growth of Highly Oriented ZnO Nanorod Arrays on Copper by a Two-Step Route AMR 1119 137–41
[9] Jayah N A, Yahaya H, Mahmood M R, Terasako T, Yasui K and Hashim A M 2015 High electron mobility and low carrier concentration of hydrothermally grown ZnO thin films on seeded a-plane sapphire at low temperature Nanoscale Res Lett 10 7
[10] Azzez S A, Hassan Z, Hassan J J, Alimanesh M, Rasheed H S, Sabah F A and Abdulateef S A 2016 Hydrothermal synthesis of highly crystalline ZnO nanorod arrays: Dependence of morphology and alignment on growth conditions International Conference On Nano-Electronic Technology Devices And Materials 2015 (IC-NET 2015) (Selangor, Malaysia) p 020034

[11] Barreca D, Bekermann D, Comini E, Devi A, Fischer R A, Gasparotto A, Maccato C, Sada C, Sberveglieri G and Tondello E 2010 Urchin-like ZnO nanorod arrays for gas sensing applications CrystEngComm 12 3419

[12] Li W, He G, Shao J, Liu Q, Xu K, Hu J and Parkin I P 2015 Urchin-like MnO2 capped ZnO nanorods as high-rate and high-stability pseudocapacitor electrodes Electrochimica Acta 186 1–6

[13] Cheng C, Zhang H, Ren W, Dong W and Sun Y 2013 Three dimensional urchin-like ordered hollow TiO2/ZnO nanorods structure as efficient photoelectrochemical anode Nano Energy 2 779–86

[14] Kurniawan R, Ittikhad A A, Sofa N A, Astarini N A, Lestari K D, Novita L R, Zulianti I, Mufti N and Rusydi A 2020 Study on optical absorption and conductivity of hybrid ZnO nanorod/graphene Proceedings Of The 3rd International Seminar On Metallurgy And Materials (ISMM2019): Exploring New Innovation in Metallurgy and Materials (Tangerang Selatan, Indonesia) p 030011

[15] Nath D, Singh F and Das R 2020 X-ray diffraction analysis by Williamson-Haller, Halder-Wagner and size-strain plot methods of CdSe nanoparticles- a comparative study Materials Chemistry and Physics 239 122021

[16] Fujiwara H 2007 Spectroscopic Ellipsometry: Principles and Applications (England: John Wiley & Sons)

[17] Barsoum M W 2003 Fundamentals of ceramics (Bristol and Philadelphia: Institute of Physics Publishing)

[18] Rao L, Zhu L B, Hu Q Y and Li X L 2012 The Influence of Pore Defects Distribution Characteristic on Casting Service Performance and Fatigue Life AMR 476–478 2530–3

[19] Serrano-Munoz I, Buffiere J-Y, Molko R, Verdu C and Nadot Y 2017 Location, location & size: defects close to surfaces dominate fatigue crack initiation Sci Rep 7 45239

[20] Yadav R S and Pandey A C 2009 Micro-Raman and photoluminescence study of urchin-like ZnO structure assembled with nanorods synthesized by hydrothermal method Struct Chem 20 1093–7

[21] Zhou Y, Liu C, Li M, Wu H, Zhong X, Li D and Xu D 2013 Fabrication and optical properties of ordered sea urchin-like ZnO nanostructures by a simple hydrothermal process Materials Letters 106 94–6

[22] Wang Y, Yang J, Jia H, Yu M and Jin H 2016 Self-assembled urchin-like ZnO nanostructures fabricated by electrodeposition-hydrothermal method Journal of Alloys and Compounds 665 62–8

[23] Chen J, Li D, Yang J, Lv X and Wang Y 2017 Facile synthesis of urchin-like ZnO nanostructures with enhanced optical properties J Mater Sci: Mater Electron 28 1605–11

[24] Hou K, Li C, Lei W, Zhang X, Yang X, Qu K, Wang B, Zhao Z and Sun X W 2009 Influence of synthesis temperature on ZnO nanostructure morphologies and field emission properties Physica E: Low-dimensional Systems and Nanostructures 41 470–3

[25] Mufti N, Maryam S, Fibriyanti A A, Kurniawan R, Fuad A, Taufiq A and Sunaryono 2018 Morphological Modification and Analysis of ZnO Nanorods and Their Optical Properties and Polarization Scanning 2018 1–8

Acknowledgment
This research was partly supported by PNBP 2020 research program from Universitas Negeri Malang. The authors thank Dr. E. Nurfani for discussions and technical works.