Effects of seeding temperature and growing time on the nanostructural characteristics of ZnO nanorods thin films prepared by chemical bath deposition

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Abstract. ZnO nanorods have been attracting much interest of researchers owing to their unique properties and extensive potential for various applications including light-emitting diode, dye-sensitized solar cells, and field-effect transistor. For being applied on those strategic applications, some basic nanostructural characteristics of ZnO nanorods such as crystallite size and the band gap energy are essential since they play important role in the device performance. In this study, the effect of seeding temperature and growing time on the nanostructure characteristics of ZnO nanorods were investigated. The seed solutions were initially prepared at the temperature of 0, 30, and 60℃ for 1 hour by using zinc nitrate tetrahydrate and hexamethylenetetramine as precursors. The ZnO seed layers were subsequently deposited onto ITO glass substrates by spin coating technique before the chemical bath deposition (CBD) growth at temperature of 90℃ for three different growth times (3, 4, and 5 hours). The synthesized ZnO nanorods were characterized by field-emission scanning electron microscopy, x-ray diffraction, and ultraviolet-visible spectrophotometry. The results showed that with the increase in seeding temperature from 0 to 60℃, the crystallite size decreased from 61.83 to 51.54 nm, while the band gap energy increased from 3.36 to 3.57 eV, respectively. On the other hand, with increase of growing time during CBD, the crystallite size was increased from 51.54 to 75.17 nm, and the band gap energy was consequently found to decrease from 3.57 to 3.46 eV. Considering the observed results above, the low seeding solution temperature and CBD growth time control are promising to optimize various applications performance required to have remarkably high crystallinity and low band gap energy.

1. Introduction
The various superior properties produced by nanometer-scale materials have recently motivated researchers to develop Zinc oxide (ZnO) nanostructures for various applications. This has increased the number of publications related to these materials to date [1]. Various types of ZnO nanostructures have been successfully synthesized including nanorods, nanocombs, nanoflowers, nanobelts, nanospirals, nanorings, nanowires, hollow spheres, and tetrapods [2]. One-dimensional ZnO nanostructures, especially nanorods, are reported to have unique physical and chemical properties that bulk materials do not have. Their properties have been extensively investigated in a wide range of applications such as dye-sensitized solar cells [3], field-effect transistor [4], and light-emitting diode [5].

Among the various fabrication methods, the chemical bath deposition (CBD) method has been massively used to grow ZnO nanorods because it can be carried out at low process temperatures without vacuum and complicated equipment. Thus, this method is simple, inexpensive, and has the potential to
produce a thin film at a low cost on a large scale [6]. Previous studies have shown that CBD synthesis parameters such as seed solution concentration [7] and seed layer [8] can influence the nanostructure characteristics of ZnO nanorods thin films such as growth orientation, density, and crystallinity which then affect the electrical and optical properties of these films. However, the study of the effect of seeding temperature on the nanostructure characteristics of ZnO nanorods thin films is still lacking.

In the present work, ZnO nanorods thin film layers were deposited on an indium tin oxide (ITO) glass substrate using spin coating method and grown via CBD. The effects of CBD synthesis parameters (i.e. seeding solution temperature and growing time) on the nanostructure characteristics of synthesized ZnO nanorods are discussed in this paper.

2. Materials and methods
The seed solution with an equimolar concentration of 0.015 M was prepared by dissolving 0.392 gr zinc nitrate tetrahydrate (Zn(NO$_3$)$_2$·4H$_2$O, Merck) and 0.21 gr hexamethylenetetramine (C$_6$H$_{12}$N$_4$, Merck) into a beaker glass containing 100 ml of deionized water. The seed solution was first prepared at the temperature of 0, 30, and 60°C and coded as ST0, ST30, and ST60, respectively. Subsequently, 150 μl of the seed solution was dripped slowly on the conductive part of the ITO glass substrate and held for 10 minutes. Then, the glass was rotated at 2000 rpm for 10 seconds and heated in the muffle furnace at 200 °C for 5 minutes. These processes (see Figure 1a–d) were carried out three times. Furthermore, the glass substrate that had been coated with seeds through a series of spin coating processes was hung vertically in a beaker glass containing seed solution as shown in Figure 1e, then stored in an oven at 90 °C with a growth time variation of 3, 4, and 5 hours. A field-emission scanning electron microscopy (FESEM JEOL JIB 4610F), x-ray diffraction (XRD) (Shimadzu X-Ray Diffractometer 7000; Cu Kα radiation λ = 1.5418 Å), and ultraviolet-visible (UV-Vis) spectrophotometry (Shimadzu 2450) were used to characterize the surface morphology, structural, and optical properties of the synthesized ZnO nanorods thin films.

![Figure 1. Schematic diagram of ZnO nanorods preparation procedure.](image)

3. Results and discussions

3.1. Morphological analysis
The morphology of the ZnO nanorods thin films synthesized with different seeding solution temperatures (0, 30 and 60 °C) and grown by CBD at 90 °C for 3 hours are shown in Figures 2a–c. It shows that the ZnO nanorods have hexagonal shapes with diameters ranging from 54.99–333.17 nm. In general, the ZnO nanorods with seeding temperature of 0°C (ST0) grew perpendicularly on the ITO glass substrate as shown in Figure 2a–b. However, the samples with seeding temperature of 30 (ST30) and 60°C (ST60) have a relatively random growth direction and were more fulfilled by nanorods which grew on a-b plane causing more nanorods collided each other. Furthermore, the diameter of the ZnO nanorods increased as the seeding temperature decreased. The average diameter of ZnO nanorods was approximately 109.42, 128.99, and 198.83 nm for the samples with seeding temperature of 0, 30, and 60 °C, respectively.

Furthermore, the FESEM images of ZnO nanorods prepared at the seeding temperature of 60°C with three different growth times are shown in Figures 2c–d. It shows that the growth orientation of ZnO nanorods along the a-b plane was gradually decreased and on the other hand more dominated by the
growth in the c-axis direction which was perpendicular to the ITO glass substrate as growth time from 3 to 5 hours increased. In addition, the increase in the growth times increased the nanorod diameters, hence the spacing between them was reduced. The average diameter of ZnO nanorods for ST60 samples grown for 4 and 5 hours was approximately 235.98 and 296.37 nm, respectively.

**Figure 2.** Top-view FESEM images of (a) ST0, (b) ST30, and (c) ST60 grown by CBD at 90°C for 3 hours; and for ST60 after growth times of: (d) 4 and (e) 5 hours.

### 3.2. Structural analysis

The XRD patterns are shown in Figure 3 where each observed diffraction pattern demonstrates six predominate peaks of the hexagonal wurzite ZnO structure at 2θ ~ 32.25°, 34.94°, 36.75°, 48.11°, 57.09° and 63.61° that correlate to the crystal plane of (100), (002), (101), (012), (110), and (013), respectively, according to JCPDS card number 36–1451 [9]. It is consistent with the FESEM images shown in Figure 2. In addition, several small diffraction peaks found at 2θ ~ 21.49°, 30.58°, 35.46°, 51.02°, and 60.66° confirmed as ITO [10]. In order to investigate a preferred growth orientation quantitatively, the texture coefficient (TC\textsubscript{hkl}) was calculated using the following equation [11]:

\[
\text{TC}_{hkl} = \frac{I_{ob}(hkl)/I_0(hkl)}{N \sum_{2}^{N} I_{ob}(hkl)/I_0(hkl)}
\]

(1)

Where \(N\) is the number of peaks observed, while \(I_{ob}(hkl)\) and \(I_0(hkl)\) are the observed and standard peaks intensity of the \(hkl\) plane given in JCPDS data. The lattice plane with the TC\textsubscript{hkl} value \(\leq 1\) indicates a random growth orientation, while the TC\textsubscript{hkl} value >1 indicates a dominant lattice plane corresponding to the preferred growth orientation. The TC\textsubscript{hkl} calculation results from the samples with three different seeding temperature scales and growth times are shown in Table 1.

Figure 3a–c shows the XRD pattern for the sample synthesized by varying the seeding solution temperature. ZnO nanorods prepared at seeding temperature of 0°C (ST0) have an XRD pattern shown in figure 3a. Based on the diffraction peaks observed in the figure, the (002) plane has the highest intensity indicating the most preferred growth orientation, which is confirmed by the highest TC\textsubscript{002} value (2.521) shown in Table 1 and consistent with the previous FESEM images shown in Figure 2a. However, the other peak belong to (100) plane appear when the seeding temperature was increased from 0 to 60°C.
as shown in Figure 3a–c. In the mean time, TC_{100} regularly increases from 0.444 to 1.933, while TC_{002} slightly decreases from 2.521 to 2.017. This indicates that the preferred growth orientation in the sample with seeding solution temperature of 60°C (ST60) is not only in the c-axis direction but also in the a-b plane, hence more nanorods grew in various directions. The change in the diffraction pattern is consistent with the FESEM results shown in Figure 2c.

Figure 3. XRD spectra of (a) ST0, (b) ST30 and (c) ST60 grown by CBD at 90°C for 3 hours; and for ST60 after growth times of: (d) 4 and (e) 5 hours.

Figure 3c–d shows the XRD pattern for ST60 samples with three different growth times. In contrast to the previous conditions, the peak (110) continues to decline, while the peak (002) continues to increase with increasing CBD growth time as reported in another study [12]. The strongest [002] peak corresponding to the most preferred growth orientation and excellent crystallinity was found in the sample after 5 hours reaction. It is confirmed by the texture coefficient in Table 1. The TC_{100} values of the ST60 sample are 1.933, 0.845, and 0.217, while for (002) plane are 2.017, 2.096, and 4.913 after 3, 4, and 5 hours reaction, respectively. This phenomenon indicates that an increase in growing time can increase the preference for growth orientation in the c-axis direction so that more nanorods grow perpendicular to the substrate, which is consistent with the FESEM results shown in Figure 2e.

Table 1. Nanostructure Characteristics and Texture coefficient of ZnO nanorods.

| Seeding Temperature (°C) | Growth Times (hours) | Average Diameter (nm) | Average Crystallite Size (nm) | Texture Coefficient (TC) |
|-------------------------|----------------------|-----------------------|-------------------------------|-------------------------|
| 0                       | 3                    | 109.42                | 61.83                         | 0.444 2.521 0.311 0.814 -- 0.910 |
| 30                      | 3                    | 128.99                | 55.33                         | 1.346 2.245 0.349 0.853 0.538 0.669 |
| 60                      | 3                    | 198.83                | 51.54                         | 1.933 2.017 0.415 0.662 0.487 0.485 |
|                         | 4                    | 235.98                | 61.50                         | 0.845 2.096 0.449 0.992 0.576 0.992 |
|                         | 5                    | 296.37                | 75.17                         | 0.217 4.913 0.189 0.401 0.128 0.151 |
By using Scherrer’s equation [13], the average crystallite size of all samples was calculated and summarized in Table 1. The average crystallite size of ST0, ST30, and ST60 grown for 3 hours are 61.83, 55.33, and 51.54 nm, while for the ST60 sample grown with a growth time of 4 and 5 hours are 61.50 and 75.17 nm, respectively. In general, these results demonstrate that an increase in growing time increased the crystallinity of ZnO nanorods. However, the crystallite size tends to decrease with increasing the seeding solution temperature. This is possibly related to the agglomeration of ZnO nanoparticles in the seed solutions when the temperature was raised [14], which affected the seed layers for further heterogeneous nucleation on the ITO glass surface during the CBD growth.

3.3. Optical analysis

In this study, the optical characteristics of ZnO nanorods were analysed using UV-Vis spectroscopy. Figure 4 and 5 show the absorbance spectra of the samples with three different seeding temperatures and growth times inserted by the Tauc Plot of \((\alpha h\nu)^2\) vs \(h\nu\) to estimate the band gap energy of each sample. Figure 4 shows that the absorbance edge curves of ZnO nanorods show a slightly blue shift as the seeding temperature was increased from 0 to 60℃. On the other hand, the absorbance edge curves of ST60 show a red shift when the growth time increases from 3 to 5 hours as shown in Figure 5. By using the Tauc’s plot [15], it was found that the estimated band gap energy of ST0, ST30, and ST60 grown for 3 hours are 3.36, 3.41, and 3.57 eV, meanwhile for ST60 with growth times of 4 and 5 hours are 3.55, and 3.46 eV, respectively confirming the crystallite growth determined in the previous XRD analysis, i.e. the greater crystallite size resulted in lower band gap energy.

![Figure 4. Absorbance spectra and Tauc plot of (a) ST0, (b) ST30, and (c) ST60 samples grown via CBD process for 3 hours.](image-url)


Figure 5. Absorbance spectra and Tauc plot of ST60 samples grown via CBD process for: (a) 3, (b) 4, and (5) hours.

4. Conclusions
In this study, ZnO nanorods on ITO substrates were successfully synthesized through the CBD technique with three different seeding temperature scales and growth times. It was found that with the increase in seeding temperature from 0℃ to 60℃, the crystallite size decreased from 61.83 to 51.54 nm accompanying a decrease in the value of TC₀₀₂, whereas the band gap energy increased from 3.36 to 3.57 eV, respectively. More importantly, with the increase of growing time during CBD, the crystallite size increased from 51.54 to 75.17 nm accompanying an increase in the value of TC₀₀₂. Consequently, the band gap energy decreased from 3.57 to 3.46 eV.

Acknowledgement
This project was financially supported by the Directorate of Research and Community Services of Universitas Indonesia through the PITTA Research Grant of Universitas Indonesia, Year 2018, contract number 2370/UN2.R3.1/HKP.05.00/2018.

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