The influence of different seeds solution concentration upon chemical bath deposition process on the morphology of ZnO nanorods

L Suhaimi1,*, AH Yuwono1 and C Hudaya2

1Department of Metallurgical and Material Engineering, Universitas Indonesia, Depok, West Java, 16424, Indonesia
2Department of Electrical Engineering, Universitas Indonesia, Depok, West Java 16424, Indonesia

*Corresponding author: lalusuhaimi@gmail.com

Abstract. The unique characteristics of zinc oxide (ZnO) nanorods including high surface to volume ratio and fast electron transfer makes this material potentially applicable for various areas such as photovoltaic devices, dye-solar cells, electric field, and biomedical. In this work, the influence of different seed solution concentration on the morphology of ZnO nanorods using chemical bath deposition (CBD) method was investigated. The seed solutions with 3 different concentration of 0.005, 0.025 and 0.05 M were prepared by dissolving 1: 1 equimolar zinc nitrate tetrahydrate (Zn (NO3)2.4H2O, Merck) and hexamethylene tetraamine (C6H12N4 / HMTA, Merck) in water at 0°C for 1 hour. The formation of seed layers was carried-out by spin coating of the precursors on the glass substrate, followed with annealing at 200°C for 5 minutes. Further growth of ZnO nanorods was performed by CBD at 90°C for 3 hours. The morphology of ZnO nanorods was characterized by using field emission scanning electron microscopy (FESEM). The results showed that seeds concentration of 0.005 M formed inhomogeneous nanorods with average diameter of 161 nanometers, meanwhile 0.025 and 0.05 M has successfully formed more homogeneous nanostructures with average diameter of 205 and 427 nm, respectively. On the basis of investigation, it has been confirmed that higher concentration of seed solution provided more suitable formation of ZnO nanorods.

1. Introduction
The use of semiconductor materials has encouraged the development of technology in various areas. One of the semiconductor materials that have a very high attraction is zinc oxide (ZnO). ZnO is included as one of the inorganic compounds, and it is generally powder-shaped with white color. This material has unique characteristics such as nontoxic, transparency in the visible range, high-electrochemical stability, high thermal and mechanical stability at room, direct band gap energy of 3.37 at 273°C, high bond energy of 60 meV and easily formed into nanostructured materials. This unique property makes ZnO material widely applied as sensors [1], solar cell energy [2], laser technology [3], optoelectronics [4], and transparent conducting oxide [5].

ZnO with nanometer dimension becomes very important because it has better characteristics compared with bulk dimensions such as surface to volume ratio and fast electron transfer. This characteristic is most expected to have a significant impact on technological developments. So far there have been many methods used to formation ZnO nanostructures, specifically ZnO nanorods such as...
chemical bath deposition [6], RF sputtering [7], spray pyrolysis [8], metal chemical vapor deposition [9], vapor phase transport [10] and pulsed laser deposition [11]. Mustafa et al [12] has successfully performed the ZnO nanorods above the gold surface by varying the precursor concentrations using the hydrothermal method. However, the ZnO nanorods formation process in this research takes quite a long time.

To overcome these problems, we investigated the formation of ZnO nanorods using chemical bath deposition (CBD) method. The formation of ZnO nanorods by CBD method takes a short time, easily available equipment, very affordable cost, simple process, harmless and suitable for the manufacture of large areas of the thin film.

2. Methodology
2.1. Preparation Nanorods Seed Solutions and Layer Deposition
Prior to the preparation of ZnO nanorods seed solutions and seed layer deposition, the glass substrate (microscope slide glass) as a growth medium of ZnO nanorods was cleaned by using ultrasonic cleaners in deionized water, acetone and ethanol for 8 minutes each and dried in water. The seed solutions with 3 different concentration of 0.005, 0.025 and 0.05 M were prepared by dissolving 1: 1 equimolar zinc nitrate tetrahydrate (Zn(NO$_3$)$_2$.4H$_2$O, Merck) and hexamethylene tetraamine (C$_6$H$_12$N$_4$/ HMTA, Merck) in water at 0°C for 1 hour. The formation of seed layers was carried-out by spin coating of the precursors on the glass substrate, followed with annealing at 200°C for 5 minutes.

2.2. Growing of Nanorods with Chemical Bath Deposition Method
Growth of ZnO nanorods was performed by CBD at 90°C for 3 hours. Furthermore, the substratum was cleaned using distilled water and dried in air. The morphology of ZnO nanorods was characterized by using field emission scanning electron microscopy (FE-SEM JEOL JIB tipe 4610F).

3. Results and Discussion
Figure 1 shows the result of FESEM and the distribution size (diameter) graphic of ZnO nanorods morphology formed by different concentrations of seed solutions. From the figure, it can be seen that at the concentration of 0.005 M, ZnO nanorods are rather inhomogeneous and the diameter distribution is uneven with average diameter of 161 nanometers. Meanwhile, at the concentrations of 0.025 M ZnO nanorods were obtained with a more orderly structure and homogeneous but the crystal orientation is still not uniform. Furthermore, the distribution of diameter ZnO nanorods are rather uniform and there are an increase in the diameter size by average diameter of 205 nm. For a concentration of 0.05 M of ZnO nanorods, it can be seen that the structure of ZnO nanorods were obtained more regularly, homogeneous and uniform crystal orientation. Based on the distribution size (diameter) graphic shows the distribution diameter of 0.05 M ZnO nanorods most uniform and the diameter size increases with average diameter of 427 nm. This phenomenon is caused by the low concentration of Zn$^{2+}$ ions as Zn(OH)$_2$ formers which will then turn into ZnO as the heating decreases [12].

Figure 1. FESEM image and probability distribution curve of ZnO nanorods morphology on glass substrate by treatment of difference of seed solution concentration (a) 0.005, (b) 0.025 and (c) 0.05 M.
The chemical reactions occur during in the formation of ZnO nanorods [13-14]

\[
\text{Zn(NO}_3\text{)}_2 \rightarrow \text{Zn}^{2+} + 2\text{NO}_3
\]

\[
\text{C}_6\text{H}_{12}\text{N}_4 + 6\text{H}_2\text{O} \leftrightarrow 6\text{CH}_2\text{O} + 4\text{NH}_3
\]

\[
(\text{CH}_2)_6\text{N}_4 + \text{Zn}^{2+} \rightarrow [\text{Zn(CH}_2)_6\text{N}_4]^2^+
\]

\[
\text{NH}_3 + \text{H}_2 \leftrightarrow \text{NH}_2 + + \text{OH}^-
\]

\[
\text{Zn}^{2+} + 4\text{NH}_3 \rightarrow \text{Zn(NH}_3)_4^{2+}
\]

\[
\text{Zn}^{2+} + 4\text{OH} \rightarrow \text{Zn(OH)}_4^{2-}
\]

\[
\text{Zn(NH}_3)_4^{2+} + 2\text{OH}^- \rightarrow \text{ZnO} + 4\text{NH}_3 + \text{H}_2\text{O}
\]

\[
\text{Zn(OH)}_4^{2-} \rightarrow \text{ZnO} + \text{H}_2\text{O} + [\text{Zn(CH}_2)_6\text{N}_4]^2^+
\]

\[
[\text{Zn(CH}_2)_6\text{N}_4]^2^+ + 2\text{OH}^- \rightarrow \text{ZnO} + \text{H}_2\text{O} + \text{C}_6\text{H}_{12}\text{N}_4
\]

Initially, the precursors of zinc nitrate tetrahydrate (Zn(NO$_3$)$_2$) and hexamethylenetetramine (C$_6$H$_{12}$N$_4$/HMTA) reacted into zinc ions (Zn$^{2+}$), ammonia (NH$_3$) and formaldehyde (CH$_2$O). Ammonia is produced from a disintegrating water reaction to produce an OH$^-$ anion. The zinc ions eventually react with the OH$^-$ and ammonia anions so that from each of these reactions are formed Zn (OH)$_2^{2-}$ and Zn (NH$_3$)$_4^{2+}$. The anion OH$^-$ is the dominant factor in the formation of ZnO nanorods. Therefore, the presence of a precursor (CH$_2)_6$N$_4$ or HMTA as an anion supplier of OH$^-$ in the formation of ZnO nanorods is vital. (7). Thus, the smaller the concentration of ZnO nanorods seeds, the percentage of HMTA precursors used slightly also affect the formation of ZnO nanorods morphology.

4. Conclusion
We have investigated the influence of different seed solution concentration on the morphology of ZnO nanorods using chemical bath deposition (CBD) method. It was found that at the concentration 0.005 M, the ZnO nanorods formed were inhomogeneous and the distribution was uneven. Meanwhile, at the concentrations of 0.025 and 0.05 M, they were more orderly structure and homogeneous. Furthermore, the increasing concentration of seed solution from 0.005 to 0.05 M has increased the average diameter ZnO nanorods from 161 to 427 nm.

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References
[1] Kumar R, Al-Dossary O, Kumar G and Umar A 2015 Nano-Micro Lett 7 97
[2] Mahmood K, Swain BS and Amassian A 2015 Adv Energy Mater 5 1500568
[3] Znaidi L, Illia G S, Benyahia S, Sanchez C and Kanaev A 2003 Thin Solid Films 428 257
[4] Antony A, Pramodini S, Poornesh P, Kityk I, Fedorchuk A and Sanjeev G 2016 Opt Mater 62 64
[5] Dosmailov M, Leonat L N, Patek J, Roth D, Bauer P, Scharber M C, Sariciftci N S and Pedarnig J D 2015 Thin Solid Films 591 97
[6] Sholehah A, Yuwono A H, Sofyan N, Hudaya C and Amal M I 2017 Int J Technol 8 651
[7] Yoo I H, Kalanur S S, Lee S Y, Eom K, Jeon H and Seo H 2016 RSC Adv 6 82900
[8] Shinde S, Patil G, Kajale D, Gaikwad V and Jain G 2012 J Alloys Compd 528 109
[9] Ye Z, Wang T, Wu S, Ji X and Zhang Q 2017 J Alloys Compd 690 189
[10] Mofor A C, Bakin A S, Elshaer A, Fuhrmann D, Bertram F, Hangleiter A, Christen J and Waag A 2006 Phys Status Solidi C 3 1046
[11] Karnati P, Haque A, Taufique M and Ghosh K 2018 Nanomater 8 62
[12] Mustafa M, Iqbal Y, Majeed U and Sahdan M 2017 AIP Conf Proc 1788 030120
[13] Wang M, Ye C-H, Zhang Y, Hua G, Wang H-X, Kong M-G and Zhang L-D 2006 J Cryst Growth 291 334
[14] Wu X, Chen H, Gong L, Qu F and Zheng Y 2011 Nanosci Nanotechnol 2 035006