Effect of the Seeding Thickness on the Growth of ZnO Nanorods prepared by CBD

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Abstract. Zinc Oxide (ZnO) nanostructure (NS), with nanorods (NRs) forward-facing alignment were deposited by chemical bath deposition (CBD) method on seeded glass substrates. Two different ZnO seed layer thickness, 100 nm and 200 nm, prepared by RF sputtering were employed to investigate the effect of seed layer thickness on the characteristics of the grown ZnO NRs. The investigations on physical, structural, and optical properties were carried out through field emission scanning electron microscope (FESEM) with integrated energy dispersive X-ray (EDX), X-Ray Diffraction (XRD), and UV and visible (UV-Vis) analyses. The morphological results reveal that with a thicker seed layer, the grown NRs diameter increased double while the NRs height was maintained at 1.5 μm. From EDX, the stoichiometric ratios of Zn:O were mostly towards 1:1. While the XRD evaluates that the preferred structure was wurtzite hexagonal with c-axis orientation along (002) plane. The UV-Vis analysis showed the increased in optical band gap energy closes to the bulk ZnO at 3.37 eV, for the ZnO NRs grown on the thicker seed layer. The obtained results illustrated high quality single-crystal ZnO NRs with different diameters were realized by only adjusting the seed layer thickness.

1. Introduction
ZnO nanorods enticed much attention as metal oxide nanoparticles with a wide direct bandgap, 3.37 eV, large exciton binding energy, 60 meV, inherent toxicity, as well as peculiar physical, chemical and optical properties. With this high specification ability, ZnO is considered as one of the preferred materials in optoelectronic, photonics, electronics and biomedical field [1-3].

There are numerous processes to fabricate ZnO materials. Deposition on a blank substrate such as glass without any pre-treatment leads to the formation of the lower density of ZnO NS and the non-supportive seeding leads to the random growth of NRs. Several studies presented the useful of the seed layer such as it plays the role as a template for the NRs [4], intended for growth parameter alignment [5], aiming for growth quality [6], decrease the nucleation edges by reducing the interface energy [7] and so on. Numerous works verify the seeding and the growth techniques via variety method had been published such as sol-gel with hydrothermal [8], spin-coating with CBD [9], spin-coating and hydrothermal [10], RF sputtering and hydrothermal [4,11,12], RF sputtering and thermal evaporation [13] and many more. The seed layer acts as a nucleation site to assure the formation of a high density of ZnO NS, assent for preferred or self-organized growth orientation increase and attend on well structural as well as optical properties likewise the bulk ZnO. RF sputtering was chosen as it promotes a large deposition area with easy proceeding and low-time consuming.
Thus, this work presents the growth control techniques employed by RF sputtering for variation of seed layer thickness, while CBD methods intended for well-aligned growth and high-quality growth of ZnO nanostructures.

2. Methodology

2.1. Preparation of seed layer
RF sputtering process was carried using Auto HHV 500 Sputter Coater with RF power of 150 W, using the ZnO target, at the base pressure of 5.5 x 10^-5 mbar and coating rate of 0.6 Å/s, as shown in Fig. 1a and large deposition area of sputtering coating plate as in Fig. 1b. Two samples with different seed layer thickness at 100 nm and 200 nm were prepared on glass substrates. Then the samples were annealed in a furnace at 400°C for 1 hour.

2.2. Growth of ZnO nanorods
The annealed seed layer was then pursued for nanostructures growth via CBD at temperature 96 oC for 3 hours. The concentration of both CBD reactants, HMTA and Zn(NO3)2 was fixed to 0.10 M as 1:1 ratio. Then the samples were annealed in the furnace at 400°C for 1 hour.

2.3. Characterization of ZnO Nanorods
The morphology, growth rate, structural, optical, properties were analysed thru FESEM (Nova Nano SEM 450, FEI, Japan with EDX), XRD (PANalytical X’pert, PRO MRD PW3040, Netherlands), and UV-Vis (Cary 5000, Agilent, US). Image processing software, ImageJ was employed to analyse the acquired images, while some equations were utilized to reveal the NS properties.

Fig. 1: (a) Schematic diagram of Auto HHV 500 Sputter Coater with RF power, and (b) sputtering coating plate with large deposition area for glass substrates.

3. Results and Discussion

3.1. Morphology by FESEM
As shown in Fig. 2a and Fig. 2b, FESEM images reveal the top morphology of the grown ZnO 1-D nanostructures. It shown that there was a significant change in size when the ZnO NRs were grown on 200 nm seed layer as compared to 100 nm. With the former seed layer twice size thicker, compared to
the later, as can be seen the resulting NRs were almost double in diameter size. However, the length of the NRs for both samples was maintained close to 1.5 μm on average. This was due to the nature of the chemical synthesis of CBD process as it reached the saturated condition, the maximum height is achieved. Elemental analysis from the EDX integrated with the FESEM as tabulated in Table 1, reveals the atomic percentage for both samples was quite close to 1:1 ratio with 56% of Zn and 44% for O, in overall.

3.2. Density Distribution by ImageJ
ImageJ software was used to analyse and to identify the growth density of the NRs from the morphology of the FESEM images. As can be seen from Fig. 3, the density distribution of NRs grown on 100 nm seed layer is given by 113/μm² (Fig. 3a), and the number is much less on 200 nm seed layer at 24/μm² (Fig. 3b). It was well understood that larger sizes of ZnO NRs on 200 nm seed layer encourage faster nucleation process. The increase in crystallite size, effectively and promoting the growth of larger ZnO NRs, while reducing the numbers of NRs on a surface area of 1 μm x 1μm [14].

3.3. Structural properties by XRD
The XRD analysis provides the structural properties of the grown ZnO NRs for diffraction angle 2θ = 20° – 80°, with ZnO reference code of 01-080-0075 as the indicator. As shown in Fig. 4, the dominant
peaks were at 34.425° and 34.375°, very close to the standard lattice constant for unstrained ZnO, $hkl$ position of 002 at 34.40°. As can be seen, ZnO NRs grown on 200 nm seed layer reveal a sharper peak, thus smaller full width half maximum (FWHM), which commonly correlated to the improvement of the ZnO crystal quality and related to the enlargement of the grain size [15,16]. Details on the data analysis has been tabulated in Table 1. From the data, both samples show that the NRs grown preferentially along $c$-axis, perpendicular to the substrate surface, which equivalent to (002) hexagonal close-packed (hcp) character, and this agrees well with the FESEM results. There is also a small shift, considerably affect the strain percentage implies to value of ±0.07% for both samples and these was caused by tensile strain and compressive strain in the ZnO NRs.

![Fig 4. XRD plot of the grown ZnO NRs on the seed layer with a thickness of 100 nm (bottom), and 200 nm (top).](image)

3.4. Diffused Reflectance UV-Vis Spectra and Kubelka-Munk Function
The optical properties of ZnO NRs were characterized using diffuse reflectance UV-Vis spectra in the range from 200 nm to 600 nm for both samples. As depicted in Fig. 5a, the grown ZnO NRs reflectance peaks show a blue-shifted characteristic for sample grown on 100 nm seed layer to 200 nm seed layer, with their peak shifted from 383 nm to 377 nm, respectively. This progressive observation was attributed to the increase in particle size [17]. Due to the larger particle size, the arrangement of atoms for the NRs follows the long range order of ZnO thus absorb towards smaller wavelength (higher energy) as the properties of bulk ZnO [18]. These data were pursued for Kubelka-Munk function analysis to determine the optical energy bandgap ($E_g$) of the ZnO NRs by extrapolating the plot to the $x$-axis as in Fig. 5b. The acquired values of the $E_g$ were found to be, respectively at 3.10 eV and 3.16 eV, and this was towards the $E_g$ of bulk ZnO. As listed in Table 1, the increase in the $E_g$ value was observed due to the smaller crystallites size of the former sample having a smaller energy gap, as compared to the to the
This work revealed the thicker seeding thickness from 100 nm to 200 nm enhances the structural and optical properties of the grown ZnO NRs by CBD. FESEM analysis shows the well-aligned, same-

![Figure 5](image-url)

**Fig. 5:** (a) Diffused reflectance UV-Vis spectra of the grown ZnO NRs, and (b) plot of K-M function.

| Table 1. Overall analysed data from FESEM, EDX, XRD, and UV-Vis from the ZnO NRs. |
|-------------------------------|-----------------|----------------|-----------------|-----------------|
| **Result by FESEM and EDX**   |                 |                |                 |                 |
| NRs grown on seed layer thickness, (nm) | Average diameter, (nm) | Thickness CS (µm) | % Atomic, (%) | % Weight, (%) |
| 100 nm                        | 48.70           | 1.574          | 0 – 43.51      | Z – 56.49      |
| 200 nm                        | 90.86           | 1.542          | 0 – 43.57      | Z – 56.25      | Z – 84.11 |
| **Result by XRD**             |                 |                |                 |                 |
| NRs grown on seed layer thickness, (nm) | Peak position, 2θ, (°) | FWHM            | D, (nm)        | Lattice strain, (%) |
| 100 nm                        | 34.425          | 0.13°          | 41.91          | 0.07           |
| 200 nm                        | 34.375          | 0.16°          | 44.60          | -0.07          |
| **Result by UV-Vis spectra and K-M plot** |                 |                |                 |                 |
| NRs grown on seed layer thickness, (nm) | Energy band gap, (eV) |                 |                 |                 |
| 100 nm                        | 3.10            | 100 nm         | 3.16            |

4. Conclusion
This work revealed the thicker seeding thickness from 100 nm to 200 nm enhances the structural and optical properties of the growth of ZnO NRs by CBD. FESEM analysis shows the well-aligned, same-
height NRs morphology for both samples with the diameter size varies from 40.7 nm to 90.86 nm. XRD analyses revealed the intense and dominant peak at $2\theta = 34.375^\circ$ for ZnO NRs on 100 nm seed layer, compared to $2\theta = 34.425^\circ$ for ZnO NRs on 200 nm seed layer. It proved the ZnO NRs high quality of crystallinity through the sharp peaks. From UV-Vis and K-M analysis, the $E_g$ was found to increase from 3.10 eV to 3.16 eV as the seed layer thicker. These values were towards the $E_g$ of bulk ZnO at 3.37 eV. The seed layer introduced by RF sputtering in this work is found to be incorporated well with the CBD method, yields to good structural and optical quality of the ZnO NRs. The outcome of this result potentially to be utilized to study the dependence of ZnO NRs geometry in optoelectronic device performance.

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References
[1] J. Kong, “Development of ZnO based light emitting diodes and laser diodes,” 2012.
[2] J. Jiang, J. Pi, and J. Cai, “The advancing of zinc oxide nanoparticles for biomedical applications,” Bioinorg. Chem. Appl., vol. 1155, p. 1019, 2018.
[3] O. F. Farhat, M. M. Halim, N. M. Ahmed, and M. A. Qaeed, “ZnO nanofiber (NFs) growth from ZnO nanowires (NWs) by controlling growth temperature on flexible Teflon substrate by CBD technique for UV photodetector,” Superlattices Microstruct., vol. 100, pp. 1120–1127, 2016.
[4] H. Ghayour, H. R. Rezaie, S. Mirdamadi, and A. A. Nourbakhsh, “The effect of seed layer thickness on alignment and morphology of ZnO nanorods,” Vaccum, vol. 86, no. 1, pp. 101–105, 2011.
[5] V. Manthina, T. Patel, and A. G. Agrios, “Number density and diameter control of chemical bath deposition of ZnO nanorods on FTO by forced hydrolysis of seed crystals,” J. Am. Ceram. Soc., vol. 97, no. 4, pp. 1028–1034, 2014.
[6] Y.-Z. Gu, H.-L. Lu, Y. Zhang, P.-F. Wang, S.-J. Ding, and D. W. Zhang, “Effects of ZnO seed layer annealing temperature on the properties of n-ZnO NWs/Al2O3/p-Si heterojunction,” Opt. Express, vol. 23, no. 19, p. 24456, 2015.
[7] O. F. Farhat, M. M. Halim, N. M. Ahmed, A. A. Oglat, A. A. Abuelsamen, “A study of the effects of aligned vertically growth time on ZnO nanorods deposited for the first time on Teflon substrate,” Appl. Surf. Sci., vol. 426, pp. 906–912, 2017.
[8] H. Jin, S. Lee, Y. Yu, S. Min, H. Chul, and M. Yong, “Low-temperature hydrothermal growth of ZnO nanorods on sol – gel prepared ZnO seed layers : Optimal growth conditions,” Thin Solid Films, vol. 524, no. December 2017, pp. 144–150, 2012.
[9] L. L. Yang, Q. X. Zhao, M. Willander, and J. H. Yang, “Effective way to control the size of well-aligned ZnO nanorod arrays with two-step chemical bath deposition,” J. Cryst. Growth, vol. 311, pp. 1046–1050, 2009.
[10] K. H. Kim, K. Utashiro, Y. Abe, and M. Kawamura, “Growth of zinc oxide nanorods using various seed layer annealing temperatures and substrate materials,” vol. 9, pp. 2080–2089, 2014.
[11] A. A. Semenova, N. A. Lashkova, A. I. Maximov, V. A. Moshnikov, D. A. Kudryashov, A. M. Mozharov, V. N. Verbitsky, P. A. Somov, “Formation of ZnO nanorods on seed layers for piezoelectric nanogenerators,” J. Phys. Conf. Ser. Pap., vol. 917, no. 032022, pp. 1–7, 2017.
[12] T. S. Tlemcani, C. Justeau, K. Nadaud, G. Poulin-vitrant, and D. Alquier, “Deposition time and annealing effects of ZnO seed layer on enhancing vertical alignment of piezoelectric ZnO nanowires,” Chemosensors, vol. 7, no. 7, pp. 1–13, 2019.
[13] F. H. Alsultany, Z. Hassan, N. M. Ahmed, N. G. Elafadill, and H. R. Abd, “Effects of ZnO seed layer thickness on catalyst-free growth of ZnO nanostructures for enhanced UV photoresponse,” Opt. Laser Technol., vol. 98, pp. 344–353, 2018.
[14] A. Takeyama, S. Yamamoto, K. Kitamura, T. Yatsui, M. Ohtsu, S. H. Baek, I. K. Park,
“Formation of ZnO nanorods on seed layers for piezoelectric nanogenerators,” J. Phys. Conf. Ser. Pap., vol. 917, no. 03202, pp. 1742–6596, 2017.

[15] P. S. Shinde, H. Divi, C. Bhosale, and K. Rajpure, “Photoelectrocatalytic degradation of oxalic acid by spray deposited nanocrystalline zinc oxide thin films,” J. Alloys Compd., no. July, 2012.

[16] W. Maryam, N. M. Subhi, S. M. Saad, N. Fazrina, M. Halim, and M. Hashim, “Annealing effects on photonic band gap of ZnO nanorod grown by chemical bath deposition,” Bul. Opt., vol. 2016, no. Cvd, pp. 22–27, 2016.

[17] R. Raji and K. G. Gopchandran, “ZnO nanostructures with tunable visible luminescence: Effects of kinetics of chemical reduction and annealing,” J. Sci. Adv. Mater. Devices, vol. 2, no. 002, pp. 1–35, 2017.

[18] X. Li, X. Chen, Z. Yi, Z. Zhou, Y. Tang, and Y. Yi, “Fabrication of ZnO nanorods with strong UV absorption and different hydrophobicity on foamed nickel under different hydrothermal conditions,” Micromachines, vol. 10, no. 164, pp. 1–13, 2019.

[19] H. Sarma, D. Chakraborty, and K. C. Sarma, “Structural and optical properties of ZnO nano particles,” J. Appl. Phys., vol. 6, no. 4, pp. 8–12, 2014.