Influence of concentration on the geometry of ZnO nanostructures prepared by chemical bath deposition

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Abstract. Zinc Oxide (ZnO) nanostructures such as nanorods (NRs), nanowalls (NWs) and nanoflakes (NFs) were successfully grown on a glass substrate via chemical bath deposition (CBD) method by varying solutions concentration (0.01 M, 0.05 M, 0.10 M, 0.15 M, 0.20 M and 0.25 M). Effect of CBD concentration on the growth and morphology of ZnO nanostructures are dignified. The structural and optical properties of ZnO NRs, NWs, and NFs were investigated by Field Emission Scanning Electron Microscope (FESEM), energy-dispersive X-ray (EDX), X-Ray Diffraction (XRD), and UV-Visible (UV-Vis) analyses. Results reveal that as the CBD concentration increases, FESEM images showed differ top-down morphology of ZnO nanostructures from NRs, NWs to NFs. Likewise, the alignment of ZnO cross-section evolved from randomly oriented to vertically oriented. As revealed by EDX, the stoichiometric ratio of Zn:O were mostly towards 1:1. From XRD analyses, the preferred structure was wurtzite hexagonal with c-axis orientation along (002) plane. The UV-Vis analysis exposed the optical band gap energy closes to the standard energy gap value of ZnO at 3.37 eV. Thus, this work introduces a variable geometry of ZnO nanostructures (NRs, NWs, and NFs) grown on glass with high structural and optical quality as standard ZnO. The fabricated materials are potential candidates for investigating random lasing in ZnO from different structural geometry.

Keywords: ZnO, nanostructure, nanorods, nanowalls, nanoflakes, CBD

1. Introduction

The ZnO nanostructure has attracted substantial interest in the research community due to several remarkable optical and structural properties such as a wide direct band gap at 3.37 eV, large exciton binding energy at 60 meV, and could be prepared into numerous geometries by different synthesis techniques [1]. These include, (but not limited to) physical synthesis (metal organic chemical vapor deposition-MOCVD, hydrothermal, radio frequency or direct current sputtering), liquid phase synthesis (wet chemical methods, CBD, sol-gel process and colloidal method), and gas phase synthesis (spray pyrolysis and inert gas condensation methods) [2-4]. Amongst all, CBD is known to be one of the most versatile techniques to control growth condition. CBD methods also offer a large semiconductor deposition area by easy procedures, low cost, low processing temperature, no vacuum, catalyst-free and relatively safe (no hazardous chemicals) and do not require any application of external field or surfactant to produce preferred nanostructures with good structural and optical properties [5-8]. Considering these factors, therefore, CBD methods were chosen for the ZnO nanostructures preparation.
2. Methodology
The sample preparation was divided into several steps to grow ZnO nanostructures on top of glass substrates coated with ZnO seed layer. **Figure 1** shows the overall flow chart of each step and process. First, the glass substrates were cleaned using DI, ethanol, and acetone sequentially in the ultrasonic bath at room temperature for 10 minutes. Then, a 200 nm thick ZnO seed layer was grown on the glass substrates using RF magnetron sputtering system with 150 W power, followed by the annealing process at 400 °C for 1 hour. The next step is to grow the ZnO nanostructures by CBD technique. For the CBD solution, six different concentration of Zn(NO₃)₂·6H₂O at 0.01 M, 0.05 M, 0.10 M, 0.15 M, 0.20 M, and 0.25 M were prepared by dissolving the concentration in DI water. Separately, HMTA (C₆H₂N₄) was dissolved similarly with the same concentration. Later, both solutions were combined as 1:1 ratio in one beaker before the prepared substrates were submerged and positioned vertically inside the beaker. The beaker was then heated in an oven at 96 °C for 3 hours. After the growth process, the samples were rinsed with DI water and dried by nitrogen blow. The samples then underwent the second annealing process, again at 400 °C for 1 hour. Physical, structural and optical characterization were done using FESEM, EDX, XRD and UV-Vis respectively.

![RF Sputtering for Seed Layer (Thickness 200 nm)](image)

**Figure 1.** Flow chart for the preparation of ZnO nanostructures.

3. Results and discussion
The growth process of ZnO nanostructures through CBD technique begins with the agglomeration of the HMTA and ZnNO₃·H₂O, resulting in the formation of ZnO nanostructures at the elevated temperature. The seed layer reduces the interface energy and provides as the nucleation site for the nanostructures. **Figure 2** shows FESEM images in a planar view and a cross-sectional view of the ZnO nanostructure for six different solution concentrations. The planar view reveals that the surface morphology of the ZnO nanostructures evolves from NRs, to NWs and finally NFs. Information on average diameter, average nanorods height as well as atomic and weight percentage from EDX analysis are listed in **Table 1**. In term of atomic percentage for the ratio between Zn and O, the value was towards 22.63 nm average diameter) to sharp hexagonal top, and bigger size (90.86 nm average diameter) with highly vertical oriented. These properties were observed from the cross-sectional view. Beyond 0.10 M, the nanostructures evolved from NRs to NWs (for 0.15 M and 0.20 M) and finally became NFs (for 0.25 M). From these observations, the major variation was in the geometrical shape of ZnO nanostructures.
and the size of the nanostructures. However, the achieved height of the nanostructures was maintained at around 1.00 µm for all samples except for the sample with the lowest concentration, 0.01 M where the nanostructures were in random orientation. It showed here that the solution concentration does not affect the lateral height of the nanostructures, but rather their geometrical shape.

![Figure 2](image-url)  
**Figure 2.** Planar and cross-section morphology for ZnO NRs, NWs to NFs as the CBD concentration increases from 0.01 M to 0.25 M.

| Concentration, (M) | Mean diameter, (nm) | Height, (µm) | % Atomic     | % Weight     |
|-------------------|--------------------|-------------|--------------|--------------|
| 0.01 M            | 22.63              | 0.667       | O – 44.12    | O – 16.2     |
|                   |                    |             | Z – 55.88    | Z – 83.8     |
| 0.05 M            | 45.90              | 1.098       | O – 41.21    | O – 15.86    |
|                   |                    |             | Z – 58.79    | Z – 84.14    |
| 0.10 M            | 90.86              | 1.123       | O – 43.57    | O – 15.89    |
|                   |                    |             | Z – 56.25    | Z – 84.11    |
| 0.15 M            | 168.47             | 1.153       | O – 44.08    | O – 15.99    |
|                   |                    |             | Z – 55.92    | Z – 84.01    |
| 0.20 M            | 366.16             | 1.017       | O – 45.09    | O – 16.73    |
|                   |                    |             | Z – 54.91    | Z – 83.27    |
| 0.25 M            | 534.07             | 1.10        | O – 47.09    | O – 17.89    |
|                   |                    |             | Z – 52.91    | Z – 82.11    |
The structural properties of the ZnO nanostructures were analyzed from XRD results. As can be seen in Figure 3, the only clear peak was seen around 34.4°. This corresponds to the preferential growth direction of the nanostructures along (002). To determine the average crystallite size which related to the average diameter (D) of the crystallite columns, the Debye-Scherer formula was employed [9]:

\[
D = \frac{0.94 \lambda}{\beta \cos \theta}
\]  

(1)

where \( \beta \) is the full width at the half maximum in radians, \( D \) (m) is the crystallite size and \( \lambda \) is the X-ray wavelength (1.54 x 10^{-10} m). In the case where ZnO crystallizes are in the hexagonal wurtzite structure, the oxygen atoms are recognized in a hexagonal close-packed with zinc atoms vacating half the tetrahedral sites and zinc and oxygen atoms are tetrahedrally coordinated to each other. According to Bragg’s law [9]:

\[
n\lambda = 2d \sin \theta
\]  

(2)

where \( n \) is the order of diffraction (first order, \( n = 1 \) and second order, \( n = 2 \)), \( \lambda \) is the X-ray wavelength, and \( d \) is the spacing between planes of given Miller indices \( h, k, \) and \( l \). In the ZnO hexagonal structure, the plane spacing \( d \) is related to the lattice constants \( a \) and \( c \), as \( a = b \neq c \). Following the equation of \( c \)-axis lattice parameter of the axial height of a unit cell, as edge length, \( a = 0 \) as only (002) peak appears [10]:

\[
\frac{1}{d_{hkl}^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}
\]  

(3)

where \( d_{hkl} \) is the interplanar spacing between planes of given Miller indices \( h, k, \) and \( l \), while \( a \) and \( c \) are the lattice constants. The lattice strain of ZnO microstructures synthesized on the PS substrate along \( c \)-axis was calculated using the following equation:

\[
\% \varepsilon = \frac{c - c_o}{c_o} \times 100
\]  

(4)

where \( c_o \) was the standard values of ZnO single crystals, \( (c_o = 0.52098 \text{ nm}) \) which indicated the good quality crystalline in nature of ZnO as be represented in XRD database, \( c \) is the lattice constant of the attained ZnO by CBD method. The dislocation density (\( \delta \)), which represents the amount of defects in the sample is defined as the length of dislocation lines per unit volume of the crystal and is calculated using equation:

\[
(5)
\]
\[ \delta = \frac{1}{D^2} \]

where \( D \) is the crystallite size as from above. All the results from XRD analyses were listed in Table 2. Overall, from this XRD analyses, it is confirmed that the ZnO nanostructures grown with c-axis preferred orientation under typical growth conditions due to the lowest surface energy of the (001) or (002) basal plane in ZnO compared to growth in the (101) and (010) direction. This allocated that the most stable morphology of ZnO hexagonal structure elongated along the c-axis, whereas its crystal consists of a nonpolar plane (100), polar basal oxygen terminated plane (001), and a polar face (001) of tetrahedral Zn terminated with O [2,11]. Besides, nonappearance of any other XRD peak specifies that these ZnO nanorods are well aligned along the c-axis [7]. Table 2 also shows that as the concentration of the reactants increased, the narrowing of FWHM value confirmed that the nanostructures were more aligned and oriented along the c-axis which is related to (002) direction as presented by the FESEM images earlier. Another observation from this analysis, as the concentration increases, it showed that the crystallite size increases. While the dislocation density diminished, which concentrates on the reduction of the lattice imperfections, the lattice misfit also lessening as a result of small changes in tensile stress that acts on the surface.

**Table 2.** XRD results for ZnO NRs, NWs and NFs as the CBD concentration increases, from 0.01 M to 0.25 M.

| Concentration, (M) | 1st order, 2θ, (°) | FWHM | D (nm) | D-spacing, \( d_{hkl} \) | Lattice, c (nm) | Lattice strain, (%) | Dislocation density, (δ) |
|-------------------|--------------------|------|--------|-----------------|-----------------|-------------------|----------------------|
| **0.01 M**        | 34.4156            | 0.30996 ° 0.00541 rad | 28.01 | 0.2603 | 0.5206 | -0.08 | 0.0013 |
| **0.05 M**        | 34.4244            | 0.18977 ° 0.00331 rad | 48.89 | 0.2602 | 0.5204 | -0.11 | 0.0004 |
| **0.10 M**        | 34.4258            | 0.16869 ° 0.00294 rad | 51.54 | 0.2602 | 0.5204 | -0.11 | 0.0004 |
| **0.15 M**        | 34.4398            | 0.15872 ° 0.00277 rad | 54.71 | 0.2601 | 0.5202 | -0.15 | 0.0003 |
| **0.20 M**        | 34.4400            | 0.15532 ° 0.00271 rad | 55.92 | 0.2601 | 0.5202 | -0.15 | 0.0003 |
| **0.25 M**        | 34.4413            | 0.15131 ° 0.00264 rad | 57.41 | 0.2601 | 0.5202 | -0.15 | 0.0003 |

UV-Vis investigations were employed to determine the excitation of the photon from the valance band, (VB) to the conduction band, (CB) and to calculate the optical band-gap energy (\( E_g \)). From Figure 4a, it shows that the UV-visible spectra have high transmittance starting from 380 nm (UV) and getting higher in the visible region. The optical band gap was determined by utilizing Tauc’s equation, while the absorption coefficients, \( \alpha \) was analysed using Kubelka-Munk (K-M) equation with \( \alpha \) is directly proportional to K-M function, and \( F(R) \) in terms of diffuse reflectance \( (R) \), \( F(R) \) is given by [12-14]:

\[
F(R) = \frac{(1 - R)^2}{2R} \tag{6}
\]

where \( F(R) \) is the K-M function. The band gap determination based on Tauc’s equation is given by [15]:

\[
(F(R), h\nu)^2 = A(h\nu - E_g) \tag{7}
\]

where \( A \) is a proportionality constant, \( h\nu \) is the energy of the incident photon and \( E_g \) is the \( \text{Bandgap} \) energy. The optical energy band gap was measured as a direct band semiconductor and the energy band
gap is obtained by linearly extrapolating to the \( y = 0 \). There are several aspects that can affect the value of the \( E_g \), such as size, the temperature, dopants, defects, tensions, and the functionalization with organic surfactants \([16]\). In this work, the decreasing in the band gap energy may cause by tensions and stress in the crystalline lattice by highly packed of ZnO grown on the glass substrate as the concentration increases as shown in Figure 4b. The band gap achieved is in the range of \( (3.13 \text{ eV} < E_g < 3.24 \text{ eV}) \) which slightly smaller to the value of intrinsic ZnO, \( 3.37 \text{ eV} \). The band gap of ZnO nanostructures shows red-shifted trend compared to bulk ZnO as the concentration increases. This shift may be affected by the origination of the structural defects during the chemical synthesis, which nearer the allowed states to the conduction band in the energy band gap. It was suggested that the red-shift may be caused by the increasing size of the synthesized ZnO nanostructures \([17]\), which totally agreed with the observation from FESEM and XRD analysis earlier.

![Figure 4. UV-Vis results: a) % Transmittance, and b) \((F(R)hv)^2\) vs \(hv\) (eV) of ZnO NRs, NWs and NFs as the CBD concentration increases from 0.01 M to 0.25 M.](image)

4. Conclusion

ZnO nanostructures were successfully synthesized with different geometry (NRs, NWs, and NFs) by varying CBD reactants solution (Zn(NO\(_3\))\(_2\) and HMTA) at an equimolar ratio. The FESEM, EDX, XRD and UV-Vis were used to investigate the effect of increasing concentration on the structural and optical properties of the nanostructures. FESEM images reveal the structural evolution from NRs to NWs and finally NFs at the highest concentration. The nanostructures also evolved from randomly oriented to highly vertical oriented. XRD indicates that the structural properties of the nanostructures grew along \( c \)-axis, \((002)\) orientation and getting more aligned and oriented as the concentration increased. The optical band-gap energy revealed by UV-Vis diffused reflectance show smaller and decreasing of energy in the range of \( (3.13 \text{ eV} < E_g < 3.24 \text{ eV}) \) to the value of intrinsic ZnO, \( 3.37 \text{ eV} \). Overall, these results show that the increase in reactants concentration leads to a variety of geometrical nanostructure with good growth quality using a simple CBD method. This work aspires a quest for the investigation on random lasing effect from different ZnO nanostructure geometry.

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