Influence of the precursor and annealing temperature on the hydrothermal growth of ZnO nanostructures

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Abstract. Wet synthesis of zinc oxide (ZnO) has been reported as an effective and low cost process for large production thin films. The purpose of this project is to investigate the effect of different precursor, different concentration and annealing temperature on the growth of ZnO nanostructures. The ZnO nanostructures is synthesised via a hydrothermal process on a glass substrate and characterized using Field Emission Scanning Electron Microscopy (FESEM). The morphological changes of the nanostructures are systematically investigated as a function of precursors and concentration as well as annealing temperature. The process use two different types of precursor which are Zinc acetate dihydrate and Zinc nitrate hexahydrate.

1. Introduction
ZnO is a unique material that exhibits semiconducting, piezoelectric, pyroelectric properties, excellent chemical and thermal stability, slow electron/hole recombination as well as relatively low cost [1]. Furthermore, ZnO nanostructure with an effective morphology has a significant potential in efficient structure and performance of nanoscale devices due to the quantum restriction of charge carriers in small extent [2].

Several fabrication methods have been reported to produce these morphological structures including electrodeposition, hydrothermal and wet chemical bath deposition (CBD) [3-5]. Among these fabrication methods, the hydrothermal method is the most advantageous because it allows low temperature synthesis, it is environmentally friendly, and it encompasses a large production area. Due to the convenience and simplicity in the operation, hydrothermal method has been proven to be versatile approach for synthesis of ZnO. In this paper, we study the effect of two different types of precursor which are Zinc acetate dihydrate and Zinc nitrate hexahydrate as well as annealing temperature on the hydrothermal growth of nanostructured ZnO.

2. Experimental procedures
Glass substrate was pre-cleaned subsequently in ultrasonic bath of acetone and ethanol. ZnO seed layer were deposited on pre-cleaned glass substrate by spin-coating method. The seed solution is prepared using Zinc Acetate Dihydrate (Zn(O\textsubscript{2}CCH\textsubscript{3})\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}), Aluminium Nitrate Hexahydrate
(Zn(NO$_3$)$_2$·6H$_2$O), Monoethanolamine (MEA) and 2-Methoxyethanol (C$_3$H$_7$O$_2$). ZnO seed layer were deposited on pre-cleaned glass substrate by spin-coating method. In the first step, seed solution is prepared using Zinc Acetate Dihydrate (Zn(O$_2$CCH$_3$)$_2$(H$_2$O)$_2$), Aluminium Nitrate Hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O), Monoethanolamine (MEA) and 2-Methoxyethanol (C$_3$H$_7$O$_2$). The solution was aged for 24 hours before the spin-coating process. After each spin-coating process, the samples were dried for 10 minutes at 150 °C to evaporate the solvent. The spin-coating and drying process were repeated 5 times to obtain the desired thickness. Finally, the samples were annealed at 500 °C for 1 hour.

The synthesis of ZnO nanostructures via hydrothermal process were prepared from aqueous solutions of Zinc Acetate Dihydrate (Zn(O$_2$CCH$_3$)$_2$(H$_2$O)$_2$) and Hexamethylenetetramine (HMT: (CH$_2$)$_6$N$_4$). Another aqueous solution used were Zinc Nitrate Hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O)) and Hexamethylenetetramine (HMT: (CH$_2$)$_6$N$_4$). These precursors were mixed in a molar ratio of 1:1 in 150 ml distilled water and undergo pre-treatment at 50 °C for 30 minutes. The solution is then vigorously stirred at 250 rpm for 3 hours. After 3 hours of stirring the solution was placed into 150ml flask bottle containing sample. The flask bottle was then immersed in 95 °C water bath for 50 minutes. After 50 minutes, the sample was taken out from the flask bottle and rinsed with distilled water. The sample was then dried at 150 °C for 10 minutes and annealed at 200 °C. The same process was repeated for different annealing temperature which is 500 °C.

3. Result and discussion

3.1. Effect of different concentration

The surface morphology of ZnO nanostructures for different concentration of precursor was studied by FESEM. The samples were studied at different annealing temperature and with different type of precursor. As observed in Figure 1 and Figure 2, the size of ZnO nanostructures increased in increasing concentration and annealing temperature. At a very low concentration, 0.05 M, the size of nanorod diameter was slightly smaller compared to the nanorod grown in 0.1 M precursor solution. Guo et al. reported that the low super saturation degree is believed to be responsible for the small-diameter and the narrow size distribution of the ZnO nanorods grown in solutions with low concentration [6]. Wang et al. reported that the growth unit diffusing in the solution and adsorbing on the nuclei [7]. The obtained crystal size and shape depend on the nucleation rate as well as the crystal growth rate.

According to Li et al., different concentration of Zn$^{2+}$ precursor may result in different concentration Zn(OH)2 which is called growth unit [8]. The supply of growth units from Zn(NO$_3$)$_2$·6H$_2$O is very little, and then the zinc precursor is transported from the root regions of nanorods to the top regions because of the gradient of concentration. So at the lower concentration regions around the tops of nanorods, the growth rate of ZnO crystals is relatively slow compared with the root of nanorods, which leads to the formation of pyramid like ZnO nanorods. H. Wei et al. also conducted an experiment indicates that the diameter of the rods is decreased by decreasing the concentration of the precursor [9].

When the concentration of Zn$^{2+}$ and OH$^-$ exceed saturation, fine ZnO nuclei spontaneously formed in the solution, then the anisotropic nanoparticles of ZnO combine together urged by interfacial free energy as well as the inability of water solution. In other words, it was the “lowest-energy” theory that decided the preferential growing plane. The rule is obeyed strictly throughout the process and no branching is observed in single nanorods. The ultrasonic pretreatment of the solution mixture makes nucleus formation uniform and decreases aggregation [7]. At a higher concentration, 0.4 M, the nanorods grown on the substrate become larger resulting in flakes shape and started to embed each other (Figure 1(c) and (f)). Figure 2((c) and (f)) shows that the nanorods grow in hexagonal shape on the substrate but in hollows and irregular shapes. Guo et al. and Zhao et al. reported a similar result in which the hollow size increases when the precursor concentration is increased from 0.3 to 0.5 M [10, 11]. The irregular shapes from concentrations of 0.3 and 0.5 M can be explained by the fact that at higher concentrations, the hexagonal rods embed each other, resulting in irregular shapes. Based on
the image observed from FESEM, it can be concluded that as the concentration of precursor increase, the size of nanorod diameter will also increase.

3.2. Effect of different precursor
The exhibited sample using zinc acetate as precursor is observed to be uniformly distributed compared to the sample using zinc nitrate. Morphological structure of sample of using different type of precursor was observed as shown in Figure 1 (zinc nitrate) and Figure 2 (zinc acetate). Figure 1 show that the structure grows uniformly in hexagonal shape in increasing concentration from 0.05 M to 0.1 M but started to embed each other, forming flakes shape at 0.4 M concentration. While in Figure 2, the result shows that the structure grows in nanorods at 0.05 M and start forming dumbbell shape at 0.1 M and 0.4 M but still grow uniformly in hexagonal shape as the concentration increase. The formation of flakes in Figure 1 ((c) and (f)) is due to the acidic strength of zinc nitrate. Singh et al. reported that the different morphologies of zinc oxide obtained are because of growth rate difference pertaining to different crystallographic planes and the crystal growth rate depends on the nature of the precursor used [12]. The acidic strength of the zinc oxide precursors used in the present study, which affects the crystal growth rate, is in the following manner: nitrate > acetate. Zinc acetate being lesser acidic than zinc nitrate, resulted in a morphology with flat end hexagonal prisms possessing longer length as compared to the hexagonal prisms produced by zinc nitrate. At higher pH values, hydrolysis/condensation is uncontrolled and unselective which leads to a highly branched structure/polymer chain. At the same time, it will also generate larger interconnected particles/structure [13].

3.3. Effect of annealing temperature
For different annealing temperature, the result exhibit that, at higher temperature, 500 °C, the diameter was larger compared to the sample annealed at lower temperature, 200 °C. Figure 1 and 2 shows the comparison of the diameter size of nanorod in which for higher annealing temperature, 500 °C, the size of nanorods are larger than at lower temperature, 200 °C.

![Figure 1. FESEM image of ZnO nanorod prepared using zinc nitrate with different concentration annealed at 200 °C: 0.05 M (a), 0.1 M (b) and 0.4 M (c) and annealed at 500 °C: 0.05 M (d), 0.1 M (e) and 0.4 M (f).](image-url)
Figure 2. FESEM image of ZnO nanorod prepared using zinc nitrate with different concentration annealed at 200 °C: 0.05 M (a), 0.1 M (b) and 0.4 M (c) and annealed at 500 °C: 0.05 M (d), 0.1 M (e) and 0.4 M (f).

The condition occurs as at higher temperature, the movement of atom in the substrate increased, thereby changing the structures of ZnO nanorods. Part of nanorods start to aggregate and the average diameter of nanorods start to increase when the annealing temperature increase to 500 °C [14]. Figure 1 shows the rods that grow in smaller size and closer. Unlikely in Figure 2, in which the rod grows larger and apart from each other as the temperature increased. The changes in morphological structure of ZnO using zinc nitrate as precursor can be observed in Figure 1((a), (b) and (c)) at 200 °C and 3((d), (e) and (f)) at 500 °C. The morphological structure of using zinc acetate is shown in Figure 2((a), (b) and (c)) at 200 °C and 2((d), (e) and (f)) at 500 °C. During the annealing process at high temperature, Zhang et al. reported that, the microstructure and stoichiometric ratio of materials will change. Due to the effect of annealing treatment, the migration of grain boundaries of ZnO nanorods is stimulated and the crystalline atom gains more activation energy [15]. In this case, the activated atoms will overcome thermal barrier between crystal grains and move freely to the correct sites in the crystal lattice through diffusion. Hence, the rod-like morphology of ZnO will gradually dissolve and convert to another particle with round-edge morphology. If the temperature continuously rises up, the grains with lower surface energy will further grow larger, which results in the final nanoparticle with aggregated morphology [13].

4. Conclusion
This work discusses the morphological structure of ZnO conducted via hydrothermal process. ZnO nanostructured was synthesised using different types of precursor, different concentrations and different annealing temperature. For different types of precursor, zinc acetate result in more uniform size of ZnO nanostructures for each concentration compared to zinc nitrate. In comparison between different concentrations, the best result obtained was by using lowest concentration, 0.05 M, in which it exhibits smaller size of ZnO nanostructure compared to 0.1 M and 0.4 M concentration. Annealing temperature also affect the sizes of ZnO nanorods. The size of ZnO nanorods increased as the annealing temperature increased. At 500 °C, the size of ZnO nanostructures was observed to be bigger than the sample annealed at 200 °C. All samples with single dimension structure and good uniformity of ZnO distribution could be potentially applied in sensor applications.
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