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Experimental Study of Precursor Concentration on ZnO Nanorods: Studies on crystalline sizes

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Abstract

In this study ZnO nanorods with having clear precursor concentration with different crystalline sizes are produced. The main object of our research, the effects of the precursor concentration on the structural and morphological properties were studied in the correlation with the crystalline sizes, micro strained dislocation density of the deposited films and the obtained results are discussed herein. The ZnO nanorods with crystalline sizes have been characterized by using different characterizing techniques X-ray diffraction (XRD) and Field emission scanning electronmicroscope (FESEM), to investigate the effects of different crystalline sizes ZnO nanorods. Thin films consisting of zinc oxide (ZnO) nanorods were chemically grown by using chemical bath deposition (CBD) with different precursor concentrations over the seeded layer ZnO synthesized via spin coating. Zinc oxide (ZnO) nanorods enables to use in verity of application such as ultraviolet light emitters, detectors, thin film transistors, spintronics, self organized nanostructures applications.

Keywords: X-ray techniques; Thin films; Precursor concentration; ZnO nanorods; Structural and morphological properties.

INTRODUCTION

Increased demands for energy throughout the world, heavy consumption of fossil fuels and environmental issues such as pollutions have increased the seriousness for the use and development of renewable source technologies. Since, the fossil fuels took millions of years to form and are nonrenewable resources, rapid exhaust of such resources will leave nothing to future generation. Burning of fossil fuel has resulted in damage to the environment. The Znic oxide (ZnO) becomes very significant II-VI semiconductor material. The band gap of 3.37eV at room temperature and also large exciton binding energy of 60meV is direct of Znic oxide. Due to its characteristics non-toxicity, chemical stability, good quality electrical, optical and piezoelectric property the ZnO increasingly paying attention. Moreover, Znic oxide (ZnO) is basic to accurately control the size, shape and microstructure of ZnO for its application as optoelectronic materials utilized as a part of sunlight based cells [2], photocatalysis [3], and light transmitting diodes, gas sensors because of the qualities of ZnO firmly rely upon its morphology and microstructure. Comprehension of the development instrument and morphology controlling of ZnO nano-structures, it is basic for its applications.

The various morphology of ZnO one-dimensional nanostructures such as nanorods, nanoflowers, nanoplates, nanotubes and nanopins are proposed by money researchers. Furthermore, the researchers used different techniques such as metal-organic chemical vapor, deposition (MOCVD) ([5,6,7]), pulsed laser deposition [8], magnetron sputtering method[9], chemical bath deposition (CBD), electrochemically deposited ZnO thin films to synthesize ZnO nanostructures for preparation method of ZnO nanostructures.

Among all these techniques the CBD is very simple technique in aqueous solution; it is growing in low temperature. Moreover, CBD method has another exceptional uniqueness, like it is very simplicity of operation and low cost [10]. In this paper, we used CBD method to grow ZnO nanostructures with different precursor concentration. We discover the effect of the reactant concentration with the crystallites size.

EXPERIMENTAL

All reagents used in this experiment, including deposition of ZnO seed layer by spin coating and deposition of ZnO nanorods on ZnO seeded layer using CBD.

The synthetic procedure for ZnO nanorods was used by CBD technique. It is composed as follows: I) seeded ZnO glass substrate was suspended in the aqueous solution containing equimolar II) concentration of zinc acetatedehydrate$Zn(CH_3COO)_2$ 2) $2H_2O$ III) hexamethylenetetramine (HMTA) $(CH_2)_6N_4$(fisher scientific) the temperature of solution was kept in the close 90ºCfor three hours, It is observed that the structure of the ZnO nanorods on the ZnO seeded thin film received. It was stirred 25 mM solution of zinc acetate dehydrate $[Zn(CH_3COO)_2.2H_2O]$ for 30 minute time. The solution of zinc was put onto clean glass substrate mounted on spin coater and spun at 3000 rpm for 30 seconds which was then followed by a twenty minute air annealing at temperature 100ºC.This step of spin coating and air annealing was repeated for five times.

We used DDW to eliminate the white loosely adherent powdery particles when the substrate was then taken out follow by air protecting at temperature 425ºC for 30 minutes time. We have used three different concentration 25 and 50 mM for the structure of ZnO nanorods. Due to investigated the effect of the concentration on the Structural and morphological.

RESULTS AND DISCUSSION

The reaction for the formation of the ZnO nanorods have been speculated as follows

$$(CH_2)_6N_4 + 6H_2O \leftrightarrow 4NH_3 + 6HCHO \quad (1)$$

$$Zn(CH_3COO)_2 \rightarrow Zn^{2+} + 2CH_3COO^- \quad (2)$$

$$Zn^{2+} + 4NH_3 \rightarrow [Zn(NH_3)_4]^{2-} \quad (3)$$

$$CH_3COO^- + H_2O \rightarrow CH_3COOH + OH^- \quad (4)$$

$$4OH^- + 2Zn^{2+} \rightarrow ZnO^{cluster} + Zn(OH)_2 + H_2O \quad (5)$$

We used an X-ray Diffractometer (D8 Advance-Bruker AXS) for analysis the Crystal structure of films. The X-ray Diffractometer is used CuK_α as radiation source with $\lambda = 1.5406$ Å in 2θ range from 20 to 80 degrees.

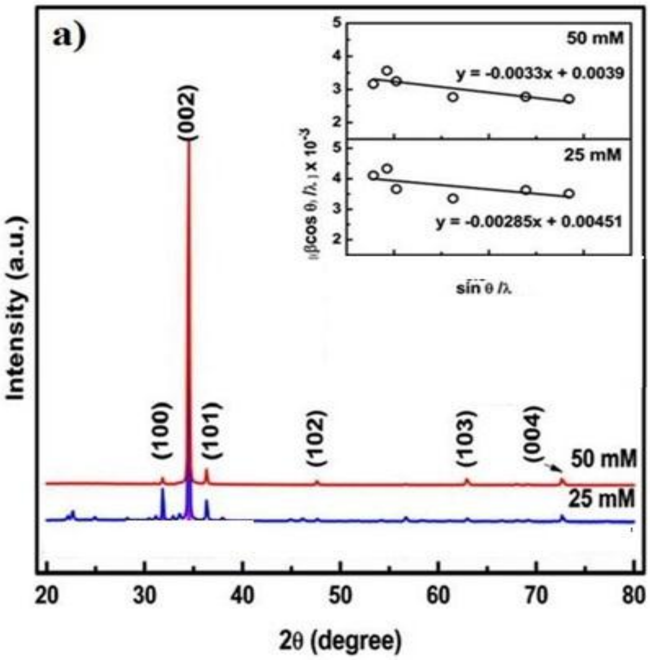

Figure 1. The typical X-ray diffraction patterns ZnO nanorods with different molar concentrations (25 and 50 mM)

Figure 1 illustrates the X-ray diffraction patterns of the CBD grown ZnO with different precursor concentrations (25 and 50 mM) and shows hexagonal wurtzite structure. It observed that the ZnO nanorods have the strongest diffraction peak (002) among the peaks 100, 103,104 that have less intensities. We used Williamson-Hall method [8], to calculate the average crystallite size with strain by the following equation:

$$\frac{\beta \cos\theta}{\lambda} = \left[\frac{1}{L}\right] + \left[\frac{\varepsilon \sin\theta}{\lambda}\right]$$

Where the strain (ε) and crystallite size (L) were related to the measured full width at half maximum FWHM (β). And λ is the wavelength of the X-Ray with the CuK_α radiation source (1.5406 Å) and (θ) is Braggs scattering angle. This method was significant, it is investigated that the peaks and give all the details information to one peak. Represents the plot between $\frac{\beta\cos\theta}{\lambda}$ versus $\frac{\sin\theta}{\lambda}$ where the slope predicts the amount of the strain, whereas the reciprocal of the intercept gives the average crystalline size is showing in figure 1. The obtained of the average crystalline size and the strain are displayed in table 1.

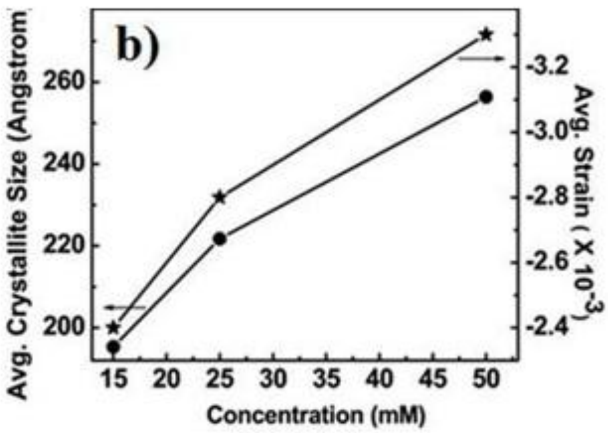

Figure 2. Williamson-Hall plot to find average crystallite size and strain analysis for different precursor concentration

Table 1: Comparative chart showing the change in precursor concentration on structural properties of ZnO nanorod thin films.

Concentration	Crystallite Size (Å)	Strain	Lattice parameter	
			Standard values	Calculated values
25 mM	221.73	-2.8×10^{-3}	c =5.20	c =5.26
			a =3.25	a =3.29
			c/a =1.60	c/a =1.59
50 mM	256.41	-3.3×10^{-3}	c =5.21	c =5.27
			a =3.25	a =3.26
			c/a =1.60	c/a =1.61

In figure 2 demonstrate the crystalline sizes were observed that the precursor concentration is improved on peaks 002. Furthermore demonstrate that the crystalline nature of the film which in turn decreases the microstrain. Williamson and Smallmans formula (i.e. $\rho = \frac{1}{L^2}$) was used to observe the trend

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of dislocation densities (ρ) with respect to the crystalline size. Precursor concentration was decreased with increasing of precursor concentration due to the changing the size of crystalline.

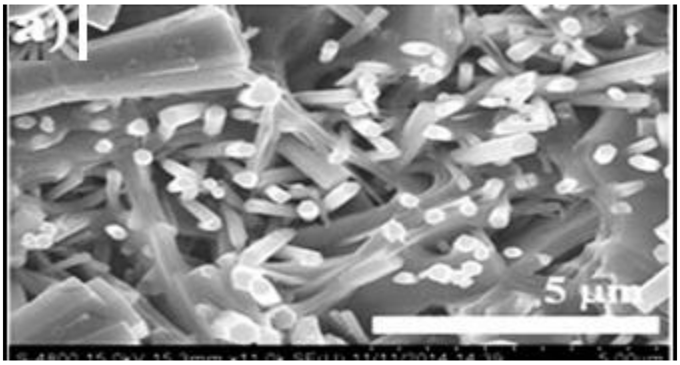

Figure 3. (FESEM) photograph of ZnO with solution concentrations as 25 (mM)

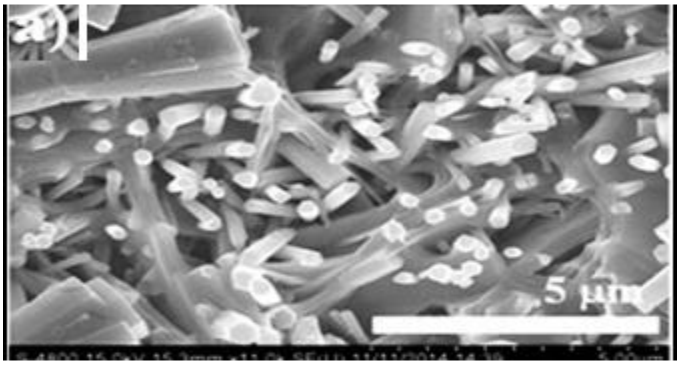

Figure 4. (FESEM) photograph of ZnO with solution concentrations as 50 (mM)

The preparation of Zno nonorods was hexagonal wurtzite structure that is demonstrated the surface morphology of the Zno film with different concentration concentrations (25 and 50 mM). it was captured by S-4800 field emission scanning electron microscopy (FESEM) operated at 15 KV is illustrated figure 3. Figure 4 shows precursor concentration of 25 mM, these Zn^{+} and OH^{-} at low concentration moves through the solution and get trapped into the active sites. It was immersed in this solution for voiding of the ZnO seed layer film. Furthermore, Zn^{+} ions at 25 mM concentration is increased result and the orientation of the nanorods is grown along with (002) plane. Therefore, the synthesised ZnO nanorods had been bigger diameter. It is observed that the big sizes nanorods bind the thin shaped nanorods.

Figure 4 demonstrates of 50 mM with higher precursor concentration. It was prepared ZnO seeded film with dip into the precursor solution of concentration 50 mM. It was observed that the thin nanorods ZnO nanorod structure is increased between thick ZnO nanorod.

Obviously, 25 mM size precursor concentration nanorods were thin with small average grain size which then it is observed that the, increase in precursor concentration. Furthermore, figure 3 the average microstrain and dislocation densities decreases with the growth of uniform nanorods which was achieved at 50 mM precursor concentration. We concluded that the FESEM figs have good correlation with the structural analysis.

CONCLUSION

In summary, by using spin coating and chemical deposition methods with simple and low cost chemical route, the ZnO nanorods over the seeded ZnO layer none were successfully employed to architect. Furthermore, it was observed that the structural and morphological properties was effecting with use different precursor concentration. The main objective was analyze the concentration the when using different crystallite size increases which can help the microstrain and dislocation density decreased.

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