Hydrothermal Synthesis and Characterization of Zno Nano Crystals

A.Ramachandra Reddy, A. N. Mallika, K. Sowri Babu, and K. Venugopal Reddy

Abstract**—**This study reports on Zinc oxide (ZnO) nano crystals prepared using zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) and sodium hydroxide (NaOH) as the starting precursors in the molar ratio's of 1:2 and 1:10 through the hydrothermal method. The effects of NaOH concentration on structural and optical properties of ZnO nano crystals were investigated. The prepared samples were annealed at 600 ˚C to obtain the ZnO nano crystals. The ZnO nanoparticles were characterized with X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FE-SEM) and UV-vis absorption spectroscopy. The hexagonal wurtzite structure of ZnO nanocrystals was confirmed from XRD results. The Full Width at Half Maximum (FWHM) of XRD peaks increased with increase of NaOH concentration which indicates that the average crystallite size of ZnO nano crystals decreased with increase of NaOH concentration. FE-SEM pictures exhibited hexagonal shaped ZnO nanocrystals comprising of cylindrical pores of diameters ranging from 9 nm to 12 nm. The number of pores as well as their diameters enhanced with increasing concentration of NaOH. Absorption spectra of these ZnO nano crystals showed an absorption peak positioned at 350 nm. This is due to the excitonic absorption in the ZnO nano crystals. The prepared porous ZnO samples using hydro thermal method may reduce the required reflection losses in the front surface which is one of the important desirable features in optoelectronic devices.

Keywords**—**ZnO nanocrystals, Hydrothermal method, Optoelectronic devices.

I. Introduction

Semiconductors with dimensions in the nano meter realm are important because of their optical and electrical properties which can be tuned by changing the size of the nanoparticles. The most common and very important property of these semiconductor nanocrystals is that their band gap varies with changes in particle size. This effect is called quantum confinement effect. ZnO is one of the wide band gap semiconductors which exhibit quantum confinement effects in experimentally accessible conditions. Zinc Oxide (ZnO) is having a wide and direct band gap of 3.37 eV and large exciton binding energy of 60 meV at room temperature [1]. Hence, ZnO finds applications in various fields such as antireflection coatings, transparent electrodes in solar cells, ultraviolet (UV) light emitters, diode lasers, varistors, piezoelectric devices, spintronics, surface acoustic wave propagation, and also in sensing of gas [2]. Various chemical synthetic methods have been developed to prepare such nanoparticles. It has been widely used in near-UV emission, gas sensors, transparent conductor and piezoelectric application [3]. Moreover, ZnO is abundantly available material, economical and it has many advantages over the GaN semiconductor which is currently being used in optoelectronic devices. However, it is very difficult to prepare p-type ZnO. If it is done, ZnO is going to replace the GaN in the near future. ZnO nanoparticles can be prepared on a large scale at low cost by simple solution - based methods, such as chemical precipitation, sol-gel synthesis and solvothermal/ hydrothermal reaction [2]. Hydrothermal technique is a promising alternative synthetic method because of the low process temperature and very easy to control the particle size. The hydrothermal process has several advantages over other growth processes such as use of simple equipment, catalyst-free growth, low cost, ease of large scale production, eco-friendly and less hazardous [4]. The low reaction temperatures make this method attractive for microelectronics and plastic electronics [5]. This method has also been successfully employed to prepare nano scale ZnO and other luminescent materials. The hydro-thermal process in general progresses in a closed system at a high autogeneous pressure. By the benefit of the closed system with high pressure, the required temperature for preparing ceramic powder can be greatly reduced because of enhanced reactivity of reactive species, and fine particles with high sinterability. In addition, the evaporation of volatile species can be suppressed, and the stoichiometry of ceramics can be maintained [6]. Ming Yang et.al has studied the effect of different precursors on hydrothermally synthesized 1-D ZnO [7]. The particle properties such as morphology and size can be controlled via the hydrothermal process by adjusting the reaction temperature, time and concentration of precursors [8].

Porous ZnO has some specific advantages such as high surface area, chemical and photochemical stability, uniformity in pore size, shape selectivity, and rich surface chemistry [9]. The high surface area of porous ZnO makes its surface more active. The highly active surface would increase the probability of interaction of gases with the semiconductor, which in turn increases the sensitivity of the material [10]. So, the material has found a variety of promising applications such as catalysts, nano-sieve filters, dye sensitized solar cells, bio- and electrochemical sensors, bone-replacement materials and also in gas sensors [9, 11, 12]. For example, for dye sensitized solar cells, ZnO thin films should be porous and have high specific surface area for exhibiting high conversion efficiency of light into current [13].

The present study focuses on the hydrothermal synthesis of ZnO nano crystals with different NaOH concentrations (1:2,

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and 1:10). The structural and optical properties of these ZnO nanocrystals were studied.

II. Experimental Section

A. Synthesis

Analytical grade zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$, 98%) and sodium hydroxide (NaOH, 97 %) were used as the starting chemicals. To prepare ZnO nano crystals, Zinc nitrate hexahydrate and NaOH were taken in required quantities and were dissolved in de-ionized water. An aqueous solution of 0.5 mol/L $Zn(NO_3)_2.6H_2O$ was mixed with the appropriate amount of 1 and 5 mol/L NaOH solution under magnetic continuous stirring to obtain the mole ratio of $Zn(NO_3)_2.6H_2O$:NaOH of 1:2 and 1:10. The final pH of the mixed solutions was highly basic with pH of 14. The mixture was put into a Teflon-lined-stainless steel autoclave unit for hydrothermal reaction at 150 °C for 7h. After hydrothermal reaction, the reactor was naturally cooled to room temperature. The obtained product was filtered, washed with de-ionized water till the pH of the final solution was 7.0. Finally the as-prepared sample was calcined at 600° C in a programmable muffle furnace at a rate of 2° C / min for 1 hr.

B. Characterization Techniques

The prepared samples were characterized with X-ray diffractometer equipped with CuK_α radiation (λ= 1.540598 Å, Model: PANalytical) to investigate crystal structure, crystallite size, strain and lattice parameters. The morphology and particle size of ZnO nano crystals were analysed by Field emission scanning electron microscope (Model: Carl Zeiss Ultra 55) and the absorption of the samples was recorded on UV-Vis spectrometer (Model: Varian, Cary 5000).

III. Results And Discussions

A. XRD Analysis

The crystal structure of the samples was investigated by analyzing the XRD data. The X-ray diffraction patterns of hydrothermal synthesized samples were shown in Fig.1. XRD spectra depicts the characteristic peaks corresponding to reflection planes (100), (002), (101), (102), (110), (103), (112) and (201) of wurtzite structure of ZnO [2]. From the Fig.1, it is clear that, the intensity of (100) reflection plane is higher than the (101) reflection plane for 1:2 NaOH concentration. In general, (101) reflection plane exhibits highest intensity for hexagonal wurtzite structure of ZnO. However, the intensity of (101) reflection peak became maximum for highest concentrations of NaOH (1:10).

The high intensity of (100) reflection plane can be attributed to the textured grain growth along (100) direction. FE-SEM pictures shown below confirm the textured growth of ZnO nanocrystals along (100) reflection plane. The similar kind of enhancement in XRD peaks was also observed in Sn doped ZnO thin films [14].

The average crystallite sizes were calculated using Scherrer's formula [15].

$$d_{xrd} = \frac{0.9\lambda}{\beta\cos\theta}$$

Where, $\beta = \sqrt{\beta_{FWHM}^2 - \beta_0^2}$ is the peak broadening after removing the instrumental broadening, $\beta_{(FWHM)}$ is the full width half maximum and β_0 is the correction factor (0.007radians). The FWHM values were also increased with increase of NaOH concentrations indicating the decrease of the crystallite size. The average crystallite size calculated for 1:2 and 1:10 of NaOH concentrations are 45 nm and 43 nm respectively (Table.1). The bond length (l) of Zn-O is calculated using the following equation [16].

Table I
The average crystallite size and the other parameters derived from XRD data.

Sample Code	D (nm)	a (Å)	c (Å)	Bond length(l) (Å)	Strain(ε)X 10^{-4}
1:2	45	0.2854	0.4944	0.17856	12.2
1:10	43	0.2855	0.4946	0.17861	12.8

$$l = \sqrt{\left(\frac{a^2}{3} + \left(\frac{1}{2} - u\right)^2 c^2\right)}$$

Where u is the positional parameter which can be expressed as $u = \left(\frac{a^2}{3c^2} + 0.25\right)$

$$a = \frac{\lambda}{\sqrt{3}\sin\theta},\ c = \frac{\lambda}{\sin\theta}$$ [17].

The calculated bond lengths were tabulated in Table.1. From the table.1, it is clear that the bond length was enhanced with increase of NaOH concentration.

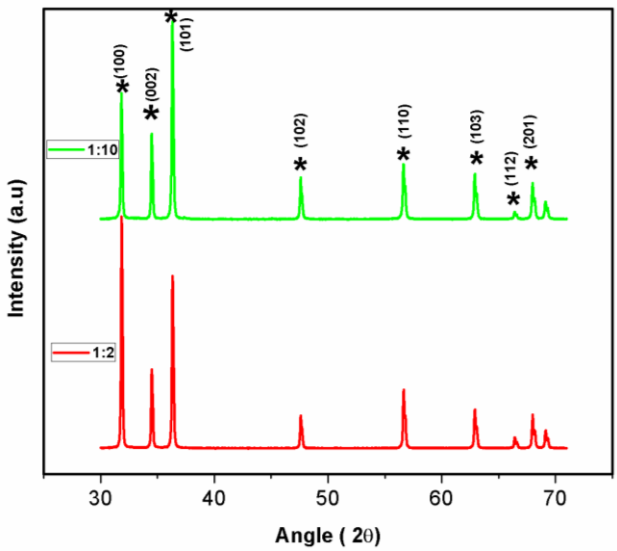

Fig.1.The XRD patterns of ZnO with NaOH 1:2 and 1:10 concentrations.

The average crystallite size and strain in nano crystals were also calculated from the spectral line shape based on

Williamson–Hall (W–H) plots and using the following equation [2].

$$\frac{\beta\cos\theta}{\lambda} = \frac{0.9}{d} + \frac{4\varepsilon\sin\theta}{\lambda}$$

Where β is the full width at half maximum, ε is the lattice strain, θ is the Bragg angle, d is the average crystallite size and λ is the wavelength of X-rays. A plot drawn between (β cosθ)/λ and (4sinθ)/λ gave rise to a straight line graph with a positive intercept as shown in Fig. 1(b). The strain is calculated from the slope of the linear fit and the intercept gives the inverse of crystallite size. It is observed from the strain plots that the strain increased with increase of NaOH concentration.

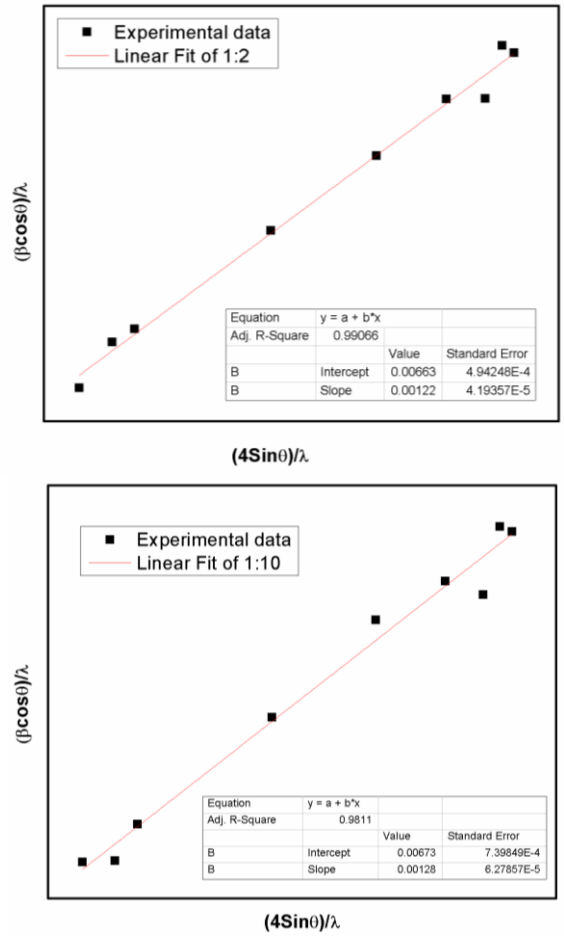

Fig.1 (b). The W-H plots for Hydrothermally synthesized ZnO nanocrystals at 1:2 and 1:10 NaOH concentrations.

B. FE-SEM Analysis

Microstructural characterization of synthesized samples was studied by FE-SEM. For morphological studies, gold coating is provided on the powder sample placed over a carbon tape. Fig. 2 depicts the FE-SEM images of ZnO nanocrystals prepared with different NaOH ratios. Fig.2 (a) and (b), shows the formation of hexagonal shaped ZnO nanocrystals. These ZnO nanocrystals contain cylindrical pores with diameters ranging from 9 nm to 12 nm. Fig.2 (d), it is evident that ZnO exhibits hexagonal shaped nanocrystals. Fig.2 (d) represents rectangular shaped ZnO nanocrystals. However, there are hexagonal shaped ZnO nanocrystals but rectangular shaped crystals are dominating. This indicates the decrease of textured growth as the NaOH concentrations increased. This confirmed the assumption made in the XRD discussion. It is also observed that, the number of pores as well as their diameters enhanced with increased concentrations of NaOH.

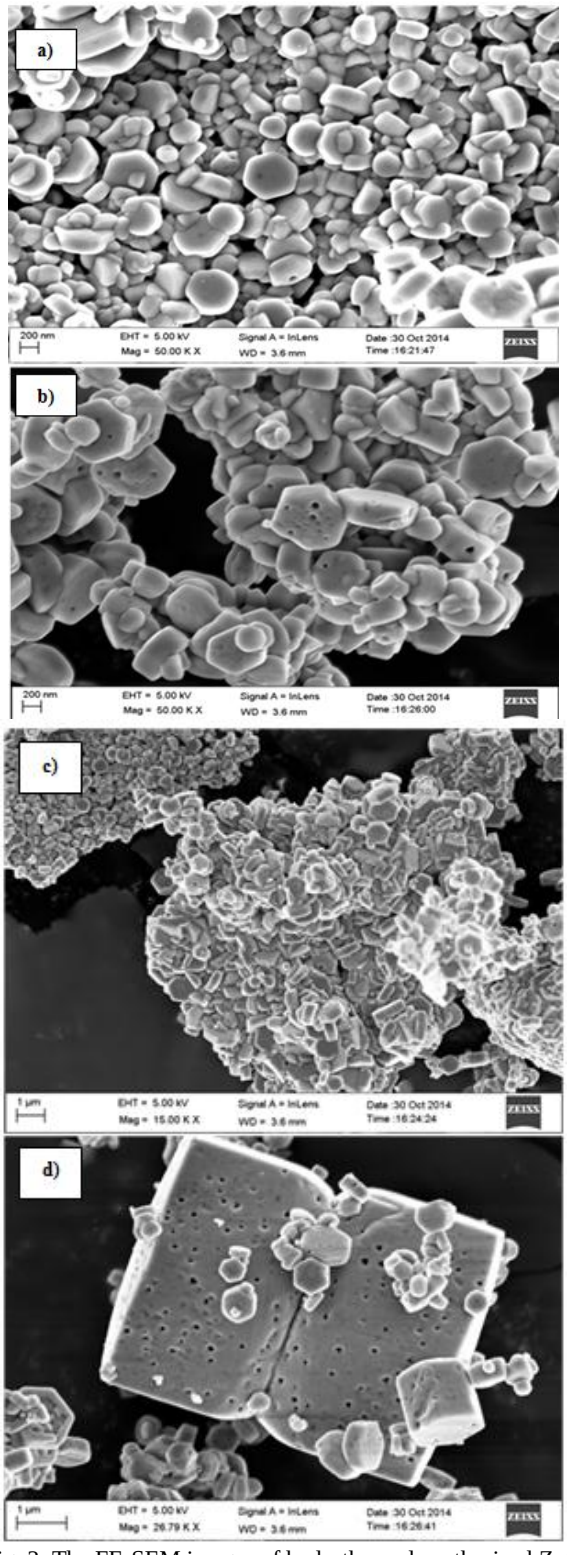

Fig. 2. The FE-SEM images of hydrothermal synthesized ZnO nanocrystals with NaOH a),c)1:2 and 1:10 b),d)

C. UV-Vis Analysis

The absorption spectra of the synthesised samples were acquired using UV-Vis spectrophotometer in the wavelength region of 200-600 nm. The UV-visible absorption spectra of ZnO nano crystals taken by dispersing them in ethanol are shown in Fig.3. The absorption depends on several factors such as band gap, Oxygen deficiency, size and structure of the nanoparticles, surface roughness and impurity centres [18].
It is observed from the figure that peak appearance in the absorption curves positioned at 350nm may be attributed to the fundamental absorption of exciton.

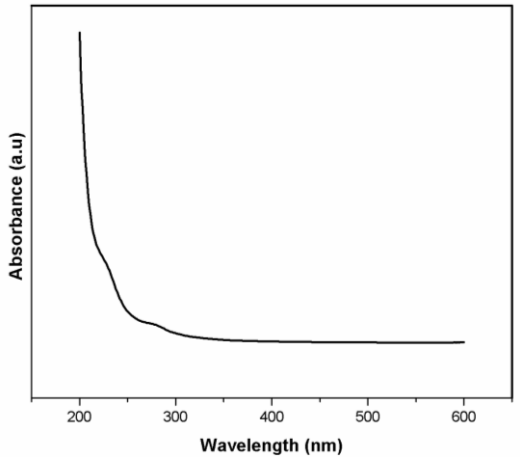

Fig.3 Absorption spectra of ZnO nanocrystals

IV. CONCLUSIONS

ZnO nano crystals were successfully synthesised by hydrothermal method by varying the NaOH concentrations. The structural and optical properties of ZnO nano crystals prepared with varying NaOH concentrations was studied. The hexagonal wurtzite structure of ZnO was confirmed from XRD studies. The crystallite size decreased with increase of NaOH concentrations. In addition to this, the (100) diffraction peak exhibited a higher intensity for NaOH with 1:2 concentration and it was assigned to the textured grain growth along (100) direction. From FE-SEM studies, hexagonal plate like morphology along with pores was observed. With increase of NaOH concentrations, the number of pores as well as the pore diameter was enhanced. The excitonic absorption was observed at 350 nm. Thus the porous ZnO prepared using hydrothermal method may reduce the required reflection losses in the front surface of optoelectronic devices which is one of the important desirable features.

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