Effect of Time Growth in Structural and Optical Characterization of Zinc Oxide Nanoparticales Synthesis by Hydrothermal Methods

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ABSTRACT

Semiconductor Zinc Oxide (ZnO) nanoparticles have been successfully synthesized by hydrothermal method by varying the growth times. The effect of growth times was investigated by means of X-ray diffraction (XRD), Increasing the time of growth has successfully increased the crystalline of the ZnO nanoparticles. The average particle size have been found to be about 50-70 nm. The absorption edge of the samples has showed and the band gap energy has been calculated.

Keywords: Band gap, hydrothermal, particle size,UV- Vis, ZnO

INTRODUCTION

In materials science, ZnO is a unique material with a direct band gap (3.37eV) and large exaction binding energy of 60meV. is a wide-band gap semiconductor of the(II-VI) semiconductor group (since oxygen was classed as an element of VI group (the 6th main group) of the periodic table and zinc, a transition metal, as a member of the IIB (2nd B), group). This semiconductor has several favorable properties, including good transparency, high electron mobility, wide band gap, and strong room-temperature luminescence. Those properties are used in emerging applications for transparent electrodes in liquid crystal displays, in energy-saving or heat-protecting windows, and in electronics as thin-film transistors and light-emitting diodes.

ZnO nanomaterials, in comparison to the bulk form ZnO, have shown novel properties for some special applications in the fields of nanoelectronics, ultraviolet lasing, frequency conversion. nanoscale optical circuitry and Geetha. so on (D. and T. Thilagavathi,2010;AzamAnarakiFirooz, et al.,2011;Hernandezbattez, A, et al. 2008;Marcel De Liedekerke, 2006). The characteristics of ZnO powder depend on its size and methods of preparation. ZnO nanoparticles can be prepared on a large scale at low cost by simple solution-based synthesis methods, such as chemical precipitation (Klingshirn, C, 2007; Wiberg, E. and Holleman, A. F. 2001, Greenwood, N. N.; Earnshaw, A. 1997). sol-gel synthesis (Spero, J. M.; Devito, B.; Theodore, L. 2000, Nicholson, J. W; Nicholson, J. W., 1998) and solvothermal/hydrothermal reaction (Ferracane, Jack L. 2001). However, agglomeration and secondary growth often occur in these ZnO nanoparticles when we dry the wet particles separated from the reaction solution. This is because large numbers of hydroxyl groups exist on the wet particle surface. 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 have several advantage over other growth processes such as use of simple equipment, catalyst-free growth, low cost, large area uniform production, environmental friendliness and less hazardous. The low reaction temperatures make this method an attractive one for microelectronics and plastic electronics. This method has also

been successfully employed to prepare nanoscale ZnO and other luminescent materials. 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.

The present study focuses on the hydrothermal synthesis of ZnO nanopowders and the effect of concentration of the precursors and time of growth on its properties. The hydrothermal synthesis of ZnO powders has four advantages (1) powders with nanometer- size can be obtained by this method (2) the reaction is carried out under moderate conditions (3) powders with different morphologies by adjusting the reaction conditions and (4) the as-prepared powders have different properties from that of the bulk(Park C.-K., Silsbee M. R., Roy D. M,1998).

Zinc oxide crystallizes in two main forms, hexagonal wuartzite and cubic zincblende. The wuartzite structure is most stable at ambient conditions and thus most common. The zincblende form can be stabilized by growing ZnO on substrates with cubic lattice structure. In both cases, the zinc and oxide centers are tetrahedral, the most characteristic geometry for Zn (W. M. HlaingOo, et al. 2005). Under conventional conditions, ZnO has the wuartzite structure, which has a hexagonal unit cell with space group C6mc and lattice parameters a = 0.3296, and c = 0.52065 nm. The oxygen anions and Zn cations form a tetrahedral unit.

EXPERIMENTAL DETAILS

In order to synthesize the ZnO nanoparticles we used raw materials ZnCl2 (0.1M) and ammonia (25%) were used for preparing the samples were calculated using the following equation

ZnCl2 + 2NH3 + H2O 2NH4Cl + ZnO(1)

By using zinc chloride (ZnCl₂) and ammonia (NH₃) precursors. Zinc chloride, 1.083 g (0.1mol), was dissolved in 80 ml distilled water, then the solution was kept under constant stirring using magnetic stirrer for half an hour to completely dissolve the zinc chloride. After complete dissolution of zinc chloride, 4 ml of ammonia solution (25%) was added under constant stirring, drop by drop. The reaction was allowed to proceed for 24 hours. After the completion of reaction the solution was poured into the crystallization vessel, which is called the autoclave, then this autoclave was heated to 90 °C in an ordinary laboratory oven, and kept in it for specific times. Subsequently, the autoclave cooled down to the room temperature normally, without using any external cooling method.

The resultant solution has been thoroughly washed with distilled water more than five times, washing carried out to remove the unwanted particles and to ensure that we got just ZnO nanoparticles. After that it was dried in the natural air, and then a white powder was obtained, then grinded for uniformities of the powder. These steps were repeated by changing the time that the autoclave has been heated for. The X-ray powder diffractometer used in the investigations of this work is a Brag- Brentano type [Y. Dimitriev, et al. 2011, Özgür, Ü., et al. 2005, Millot, Marius, et al, 2010], The data are collected then fed to the FullProf suite, in order to determine the full width at half maximum (FWHM), though to calculate the particle size using the famous Scherrer equation(Dal Corso, 1994):

Where λ is the wavelength (Cu K_a), β is the FWHM, Θ is the diffraction angle. We used the spectrophotometers and Tauc's relation equation (3) to calculate the band gap energy for the prepared nanoparticles.

 $(\alpha hv)^2 = A^2 (hv - E_g) \dots (3)$

Where A is known as the edge width parameter, hv is the photon energy and E_g is the optical gap. The Tauc plot is a method that is widely used for the determination of band gap. Shown next is the procedure for determining the band gap from a diffuse reflectance spectrum using the Tauc plot. The absorption coefficient of an incident photon α can be calculated by equation (4), from a plot of $(\alpha hv)^2$ against (hv), the optical band gap energy can be obtained (J. Tauc, R. Grigorovici and A. Vancu, 1966).

$$\alpha = lin\left(\frac{l_0}{l}\right) * d \dots (4)$$

RESULTS & ANALYSIS

X-Ray Result and Particle Sizes Calculations

X-ray diffraction data for four samples prepared at different times were recorded by using (Cu, K α) radiation of wavelength (1.5410 Ű). Figure 1 shows that XRD patterns of ZnO nanoparticles annealed at different times, the all peaks of the different samples in the same positions with small shift with different time of preparation, x-ray diffraction studies confirmed that the synthesized materials were ZnO with wurtzite phase and all the diffraction peaks agreed with the reported JCPDS data (JCPDS Card No. 36-1451)and compared this results with data published in many articles get the same position of the peaks and all the samples polycrystalline and correspond to hexagonal structure with lattice spacing a = 0.325 nm and c = 0.521 nm (Laudise, R.A, 1986).

The width of the diffraction peaks observed that decreased while the times of the treatments increase. Also intensity of sample S1 indicate that the crystallite structure was not complete yet, but the intensity of major diffraction peaks increased indicating that the crystallization of ZnO nanoparticle was improved at long time show that in samples S2, S3, and S4.

The full- width at half maximum (FWHM) on the (101) peak had a tendency to increase with annealing time increasing shown in Figure 2. In addition, our results and previous reports (Azam et al., 2009) also show that increasing the time treatment improves the crystallization of ZnO nanoparticles. To understand the crystalline mechanism of ZnO, the grain size of ZnO nanoparticles has been estimated from the FWHM of (101) the diffraction peak using the Scherrer formula (2).



Figure 1. XRD patterns of ZnO nanoparticles synthesized in various times at 150^oC, the vertical line in Lower layer indicate the Bragg's positions for the ZnO (JCPDS Card No. 36-1451)



Figure 2. The main diffraction peaks (101) for ZnO synthesis samples, used to calculate the grain size

Table 1. Structural parameters and	d particles size of ZnC) nanoparticles in	different growth time
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Sample	Growth Time/h	Angle (2Ө)	FWHM	d-spacing (A°)	Particle Size (nm)
S 1	3	36.69	0.263	2.6	54.91
S2	6	36.51	0.242	2.6	59.61
S3	9	36.49	0.215	2.6	67.10
S4	12	36.36	0.213	2.6	67.73

Table1 shown that the FWHM decreased with time increased, the particles size was increased. So we can control the size of particle by changing the growth time.



Figure 3. Variation of FWHM and grain size (nm) of ZnO nano particles synthesized at different growth times

UV Absorption Results



Figure 4. Shows the absorption edge of S2, S3, and S4 from UV-vis

Figure 4 shows the room temperature UV–vis absorption spectrum of the synthesized powder. A broad band was observed in the spectrum at ~ 370 cm⁻¹ for all samples, which is a characteristic band for the wurtzite hexagonal pure ZnO. No other peak was observed in the spectrum confirms that the synthesized products are ZnO only (Y.H. Ni, 2005).

Calculation of band gap energy (Eg)

ZnO can be described as a direct band-gap semiconductor. The original study of Tauc (J. Tauc, R. Grigorovici and A. Vancu, 1966), in which the distributions of electronic states are assumed to be exactly square-root in character, terminating abruptly at the respective band edges, leads to a simple analysis of optical absorption and luminescence experiments. Optical absorption and luminescence occur by transition of electrons and holes between electronic states such as conduction and valence bands, tail states, and gap states. Tauc's relation equation 3, describes the dependence of the optical absorption coefficient, α , on the energy gap.

The empirical determination of the optical gap E_g can then be achieved by plotting α hv vs. hv, which is known as Tauc's plot (a schematic illustration of Tauc's plot is shown in Figure 5). However, the presence of localized tail states extending from the conduction and valence bands into the energy gap makes the determination of an optical gap unclear.

The method used to calculate the optical gap by using Tauc's relation, and extrapolates the high energy, linear section of the plot of α hvvs. hv, and takes the intercept with the x-axis as the value of the optical gap, as shown in Table 2. The characteristic values for the band gap of ZnO determined from Tauc's plot range from ~3.35 eV to ~3.53 eV. The variations in gap value are due to preparation conditions for S₁, but it is well accepted that the main parameter responsible for the value of the optical gap is the time growth.Indeed, there are numerous studies that have investigated the dependence of the optical gapand other optical parameters, like absorption coefficient and refractive index.In summary, it hasbeen shown that the optical band-gap of ZnO tends to increase with time growth increase.



Figure 5. A schematic illustration of a Tauc's plot. The extrapolation of the high energy linear portion is used to determine the optical gap E_g for S1, S2, S3, and S4.

Table 2. Energy	gaps for	ZnO bul	k and	prepeared	samples	of ZnO	nanoparticles	in	different
growth time									

Sample	Growth Time /h	E _g of bulk ZnO (eV)	$E_g of ZnO (eV)$
S1	3	3.	
S2	6	2 27	3.44
S 3	9	5.57	3.40
S4	12		3.35

CONCLUSION

ZnO nanoparticles have been prepared using hydrothermal method. And the influence of processing parameter (time) on the final samples has been shown previously. The results of XRD measurements indicate that the prepared nano ZnO had a crystallite structure which is a characteristic band for the wurtzite hexagonal structure, also its have been used to calculate the particles size, which was about 54nm to 70nm which increased with times of growth, this is due to the change of growth rate between the different crystallographic planes. Ultra violet spectroscopy was used to obtain the absorption edge of the four samples and then to calculate the band gap energy for all samples, which were found decrease the band gap with particle size increased.

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