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Study of microstructure and optical band gap of ZnO nanoparticle prepared by CBD method at different molarity

Physics

KEYWORDS: ZnO nanoparticles, Semiconductors, UV–vis absorption, Optical band gap

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ABSTRACT

We report synthesis of zinc oxide (ZnO) nanoparticles via chemical bath deposition method using molarsolutions ofzinc nitrate hexahydrate [Zn(NO3)2 6H2O] and ammonium hydroxide (NH4OH) with polyvinylpyrollidone(PVP) as capping agent. The synthesized ZnO nanoparticles are characterized by X-ray diffraction(XRD) technique and Transmission electron microscopy (TEM) for compositional analysis andsurface morphology. The average crystallite size calculated from XRD pattern has been found to be on the order of 197.8 nm. To calculate the band gap UV–vis absorption spectra have been utilized. The optical band gap value of the synthesized ZnO nanoparticle is found to be on the order of 5.3eV. The size and distribution of ZnO nanoparticles has been compared by TEM.

1 Introduction

Nano-semiconductor materials have attracted much interest from researchers due to their peculiar properties which are not shown by their bulk counterparts. ZnO is a semiconductor compound which is technologically an important material due to its wide range of optical and electrical properties. ZnO nanostructure is recognized as a promising material for improving nanoscale optoelectronic devices, such as band gap engineered solar cells, organic light emitting diodes (OLED's), Ultra-violet (UV) laser diodes etc.[1,2]. For the preparation of ZnO nanoparticles different synthesis methods have been developed and among these one of the most attractive method is Chemical Bath Deposition (CBD) method due to its perfect control of morphology, purity, crystallinity, composition and low cost for large-scale production. In this work our attempt is to report the synthesis of ZnO nanoparticlefor the study of microstructure and optical band gap at different molarity.

2 Experimental

Materials: All materials for this experiment were purchased from the commercialmarket with highest purity (99.99%). For the synthesis of ZnO nanoparticles Zinc nitrate hexahydrate [$Zn(NO_3)_2$ $6H_2O$] and ammonium hydroxide (NH_4OH) were used as the starting materials . Polyvinylpyrrolidone (PVP) and double-distilled water were used as capping agent and dispersing solvent respectively.

Preparation of ZnO nanoparticles: For the preparation of ZnO nanoparticles 100 ml of 0.125 mol solution of $Zn(NO_3)_26H_2O$ was stirred constantly for 30 min at 60º C (solution A). 0 .75 wt% of PVP was stirred constantly at 60º C for 30 min (solution B). NH_4OH was slowly added drop by drop intosolution A and stirred at room temperature for 15 min. pH of the solution was continuously measured. The addition of NH_4OH was stopped when the pH of the solution was 7.5 and a white solution (solution C) of ZnO was formed. Then the final mixture (solution B and solution C) was stirred constantly for 1 h at 60º C and allowed to cool down at room temperature till the white precipitate of ZnO was formed. The whole solution was allowed to settle overnight in a darkchamber. Finally, the precipitate was filtrated and washed with distilled water to dissolve the impurities which was dried at 60º C in an oven for 12 h. Same procedure was followed for preparation of ZnO nanoparticles using 0.25 mol of $Zn(NO_3)_26H_2O$, 1.5 wt% of PVP and 0.5 mol of $Zn(NO_3)_26H_2O$, 3 wt% of PVP for controlling the size of the particle. The chemical reaction taken place for the formation of ZnO is as follows[3]

$$NH_3+H_2O\rightarrow NH_3{\cdot}H_2O\rightarrow {\cdot}NH_4^+$$

$$Zn^{2+}+4NH_3\rightarrow Zn(NH3)_4^{2+}|$$

$$Zn(NH_3)^{2+}+2OH^-\rightarrow ZnO+4NH_3+H_2O$$

$$Zn^{2+}+4OH^-\rightarrow Zn(0H)_4^{2-}$$

$$Zn(0H)_4^{2-}\rightarrow ZnO+H_2O+2OH^-$$

Characterization methods: Powder X-ray diffraction(XRD) pattern of prepared ZnO nanoparticle is recorded by a Philips X-ray Diffractrometer (X'Pert Pro) with Cu K $_1$ radiation (=1.5406 Å). The optical absorption spectra of ZnO dispersed in water are recorded by a UV–visspectrometer (HITACHI model U-3210). Transmission electronmicroscopy (TEM) observations are carried out on a JEM-100 CXII electron microscope. The band gap of the ZnO nanoparticle is calculated from the UV absorption result.

3 Results and discussion

X-ray diffraction analysis:

The phase structure and indexing of chemically grown ZnO nanoparticles are determined by comparing the peak position (2) and relative intensity of the prepared samples with the standard ICDD data base. The result shows the presence of only ZnO phase for the sample with 0.125 molarity. But the diffractograms of other two samples with molarity 0.25 and 0.5 show the presence of other crystalline structure. Figure 1(a) shows the X-ray diffraction pattern of ZnO nanocrystalline structure. All peaks correspondto the (100), (002), (101), (102), (110), (103), (200), (112), (201), and (004) planes in the hexagonal phase of ZnO with space group P63 mc and unit cell parametersa = b = 3.257 Å and c = 5.213 Å (PDF No. 79-0207). No diffraction peaks from other species could be detected, which indicates that all the precursors have been completely decomposed and no other crystal products have been retained after the decomposition process. The broadening of peaks is observed which is mainly due to the finite size (D) of the crystallite and some contribution of strain. Figure 1(b) and 1(c) show the X-ray diffraction pattern of the samples with molarity 0.25 and 0.5 in which many diffraction peaks from other species could be detected, which indicates that all the precursors have not been completely decomposed and other crystal products havebeen retained after the decomposition process. The following procedure is adopted prior to XRD observation[3]

(1) The diffractometer is calibrated by a standard silicon sample.
(2) Correction of instrumental broadening of β_{20} arising due to slitwidth of the $K\alpha_1$ and $K\alpha_2$ lines is also made. The diffraction broadening only due to grain size βg is given by the Warren rule[4]

$$\beta^2_{g=}\beta^2_2\theta-\beta^2$$

where β is FWHM of a line produced under similar geometrical conditions by the standard material (silicon) with crystallite size 54 nm. The crystallite size (D) for the chemically prepared ZnO nanoparticles is then evaluated for the preferred planes (hkl) using Debye Scherrer's formula[5]

$$D=K\lambda/\beta_g\cos\theta$$

Whereλ is the wavelength of radiation used, θ is the Bragg angleand K=0.9 for spherical shape. The average crystallite size is found to be 197.8 nm in the directions perpendicular to (100), (101), (102), (110),

(103) and (004) planes.

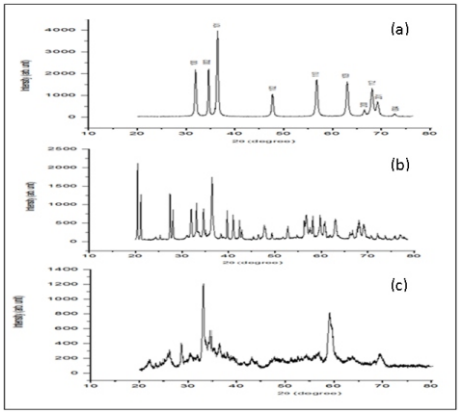

Figure. 1. X-ray diffraction (XRD) pattern of the prepared ZnO nanoparticles at different molarity

Broadening of the peak may also occur due to micro-strain developed in the crystal structure arising from defects like dislocation and twinning, etc. These defects are considered to be associated with the chemically synthesized nanocrystals because they grow spontaneously during chemical reaction. As a result the chemical ligands get negligible time to get to an energetically favourable site. In some cases it could arise due to insufficient energy that is needed for an atom to move a proper site in forming the crystallite. The information on the strain and the particle size was obtained from the FWHM of the diffraction peaks. After applying the correction for instrumental broadening, the FWHM's can be expressed as a linear combination of the contributions from the strain and particle size through the following equation[6]

$$\frac{\beta_g cos\theta}{\lambda} = \frac{\varepsilon sin\theta}{\lambda} + \frac{1}{L}$$

Where $\beta_g$is the measured FWHM in radians, θ is the Bragg angle of the diffraction peak, λis the X-ray wavelength, *L* is the effective particle size, and ε is the effective strain

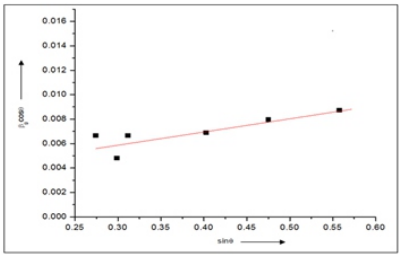

Figure. 2. Willamson–Hall plot for ZnOnanopartiles for the sample with molarity 0.125

A plot of βgcosθ versus sinθ for the sample with molarity 0.125 is shown in Figure 2. The strainis estimated from the slope of the line and the effective particle size (L) from the reciprocal of intersection with the vertical axis on βgcosθ versus sinθ plot and the average particle size is calculated. The calculated value of strain is 0.015. The crystallite size from Willamson–Hall plot and corresponding strain of the ZnO nanoparticles is 290.6 nm. XRD is widely used to determine the particle size of nanoparticles but TEM is the best way for the measurement of nanoparticle size.

Transmission Electron Microscopy (TEM) analysis:

The Scherrer method for calculating particle size gives an average value of the entire particle responsible for diffraction. However, by TEM, besides directly measuring particle size, the morphology of the particles can also be observed. The typical HRTEM result is shown in Figure.3. Almost non-dispersed, individual nanoparticles are identified as bulk dots in the HRTEM micrograph having average diameter of nanoparticle is 200 nm. It is to be noted that the HRTEM photograph pattern is recorded using selected area observations and the particle size is determined in higher magnification (~2×105). The grain boundaries (GBs) of nanograined ZnO can drastically change the physical properties [7–9]. Nanograined ZnO is considered to be an important material for applications in solar cells, sensors, photovoltaics, photocatalysis and sprintonics[10].

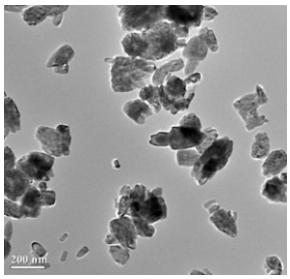

Figure. 3. TEM micrographof ZnO nanoparticles

UV-vis- Absorption Spectrometery analysis:

Uv–vis characterization: UV–vis spectra are taken from the colloidal solution of ZnO. The UV absorption spectrum is shown in Figure 4(a). The direct band gap of ZnO colloid is estimated from the graph of hν versus $(\alpha h\nu)^2$ through the absorption coefficient α which is related to the band gap Eg as $(\alpha h\nu)^2 = k(h\nu - Eg)$, where hν is the incident light energy and k is a constant .The extrapolation of the straight line in Figure 4(b) to $(\alpha h\nu)^2=0$ gives the value of band gap energy E_g. The optical band gap (E_g) is found to be size dependent and there is an increase in the band gap of the semiconductor with a decrease in particle size. The optical band gap value obtained for ZnO nanoparticle at molarity 0.125 is 5.3 eV.

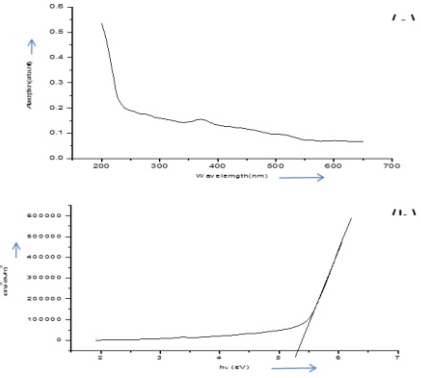

Figure. 4. (a) Absorption spectra of ZnO colloid and (b) optical band gap of ZnO colloid

4 Conclusions

ZnO nanoparticles have been successfully synthesized by chemical bath deposition method at low temperature with molarity 0.125.But X-ray diffraction pattern of the samples with molarity 0.25 and 0.5 showed many diffraction peaks from other species, which indicates that all the precursors have not been completely decomposed and other crystal products have been retained after the decomposition process. The nanostructure of the prepared ZnO nanoparticle with molarity 0.125 has been confirmed using XRD, UV–vis absorption and TEM micrograph analyses. XRD result shows that the obtained ZnO nanoparticles are composed of ZnO phase in the hexagonal system with space group P63 mc and unit cell parameters are a=b=3.257 Å and c=5.213 Å with proper crystallinity. Theaverage crystallite size obtained by XRD is 197.8 nm using the Scherrer formula. The estimated optical band gap of ZnO is found to be 5.3eV.

Acknowledgments

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