Optical Properties of ZnO Nanorods

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Abstract: *The synthesis of ZnO nanoparticles has attracted a lot of interest because of their unique properties and potential applications in optoelectronic devices. ZnO as a wide band gap semiconductor with large excitation energy and becomes one of the most important functional material with near UV-emission, optical transparency, electric conductivity and piezoelectricity. ZnO nanoparticles were prepared by hydrothermal method. The structure and morphology of the samples were investigated by X-ray diffraction and Scanning electron microscopy. X-ray diffraction revealed the hexagonal primitive structure of ZnO nanorods. Average particle size of the sample was calculated from the XRD. SEM micrographs showed the hexagonal shape of ZnO nanorods. The UV-VIS absorption spectra showed blue shift in wavelength corresponding to bulk. Band gap energy of ZnO nanorods was determined from UV absorption spectra and it confirms quantum confinement.*

Keywords: *ZnO nanorods, XRD, SEM, UV-VIS spectroscopy.*

Introduction:

ZnO is a semi-conductive oxide with wide band gap energy of 3.37 eV, large exciton binding energy of 60 meV at room temperature, a high range of resistivity (10^{-3}–10^{5} Ω-cm) and transparency in the visible wave region. Due to its environmental friendly nature, cost effectivity and controllable electrical conductivity it has been extensively studied [1] by many researchers and proved as a promising material for various applications. ZnO has been explored for many applications like solar cells [2], gas sensors [3], electrical and optical devices [4, 5], cyto-toxicity [6] and antibacterial activities [7]. ZnO nanoparticles are widely employed in fundamental research and potential applications, such as ultraviolet lasers and diodes, field emitters, piezoelectric devices and hydrogen-storage [8], controlling units as UV photo detectors, fluorescence labels in medicine and biology and as high-flame detectors [9], in cosmetic industry as a component of sun screens [10].

In the present paper the synthesis of ZnO nanorods through hydrothermal method is reported. The structural and optical properties of the prepared ZnO nanorods have been confirmed using XRD, SEM and UV-VIS absorption spectroscopy. All these results are presented in this paper.

Experimental Details:

To prepare ZnO nanorods, all the reagents used in the experiments were of analytical grade (purchased from Merck chemical industrial company) and used without any further purification. In the reaction Zinc nitrate $Zn(NO_3)_2$ was used as a precursor, hexa-methylene-tetramine ($(CH_2)_6N_4$) was used as a directing agent and distilled water as a reaction medium.

A 0.05 M stock solution of zinc nitrate and hexa-methylene-tetramine (HMT) were prepared separately in distilled water. Both these solutions were mixed by adding HMT solution

in the zinc nitrate solution. The resulting precursor suspension was transferred in the Teflon lined stainless steel autoclave of 90 ml capacity and filled 60% with reaction media one by one. Then the autoclave was maintained at desired temperature of 110 ºC for 6 hour duration. After achieving required temperature and time for reaction autoclave is air cooled to room temperature. The obtained precipitates were washed and filtered several times with distilled water by using Wattman fine filter papers to remove the water content. To remove traces of water content white powder was dried in vacuum oven at 80°C for 2h.

The phase crystallinity and particle size of the prepared nanorods were evaluated using powder X-ray diffraction (XRD) with Schimadzu LabX- 6100 powder diffractometer with an incident wavelength of 1.54 Å. The surface morphology of the as-prepared samples was inspected using the scanning electron microscopy (SEM) using a JEOL, JSM 5600 microscope at the Physics Department, SPPU, Pune. To characterize their ability to absorb visible light, the band-gap energies of all the samples were determined from the UV–vis-spectroscopy measurements carried out at the Central Facility at Garware College, Pune.

Results and discussion:

1) X-Ray Diffraction:

The detailed knowledge of the crystal structure and distribution of cations over the interstitial sites is important to understand the physical properties of that material. Such detailed structural information including cation distribution over the interstitial sites can be obtained by diffraction technique. The X-ray analysis is widely used to determine the crystal structure and the phase of the nanoparticles. The X-ray diffraction pattern is conducted in the range 10 – 80 degrees and is shown in the Figure 1. The finite width of the diffraction peaks confirms the formation of nanostructure. Well defined reflections were observed at the planes (002), (100), (101), (102), (110) and (103). These diffraction peaks match well and indexed to the JCPDS data sheet 790208 confirms the formation of ZnO. The maximum intensity of (002) peak indicates the c-axis oriented growth and confirms the hexagonal primitive lattice structure of the sample. The average crystalline size D of the as prepared nanoparticles is calculated by using Debye Scherrer's equation

$$D = \frac{0.9\lambda}{\beta Cos\theta}$$

Where, λ = wavelength of the incident light = 0.154 nm
β = full width at half maxima (FWHM) of a diffraction peak
θ = Bragg's diffraction angle.

The particle size calculated from the XRD is 81 nm for ZnO.

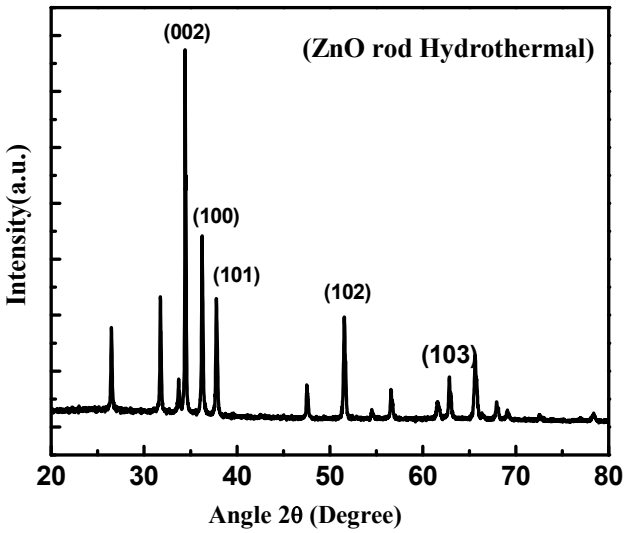

Figure 1: XRD of ZnO Nanorod structures

2) SEM Results:

The as-prepared sample was examined for the surface morphology with the Scanning electron Microscopy technique. The SEM image of ZnO nanorods is shown below. From the Figure 2 it is clearly observed that ZnO exhibits nanocrystalline nature with hexagonal rod like morphology. This is because of HMT which is a directing agent who directs the growth of the nanorods in one direction.

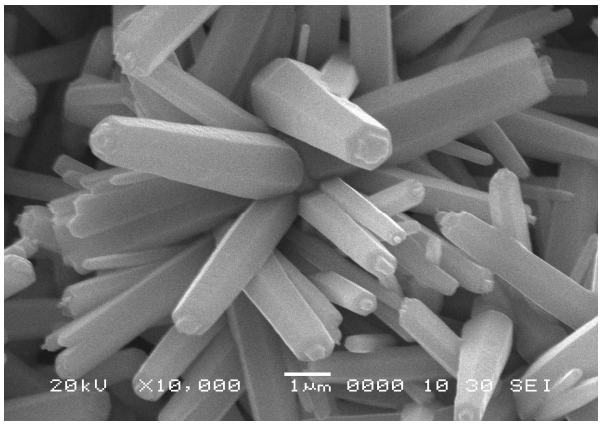

Figure 2: SEM micrographs of ZnO Nanorod structures

3) UV-VIS Absorption Spectroscopy Results:

In study of the fundamental properties of some semiconductors, the absorption by the second type of electrons is of great importance. In an ideal semiconductor, at absolute zero temperature, the valence band would be completely full of electrons so that electron could not be excited to a higher energy state from the valence band. Absorption of quanta of sufficient energy tends to transfer these electrons from valence band to conduction band. The optical absorption spectrum of semiconductors generally exhibits a sharp rise at a certain value of the incident photon energy which can be attributed to the excitation of electrons from valence to conduction band. The conservation of energy and momentum must be satisfied in optical absorption process. Basically there are two types of optical transitions that can occur at the fundamental edge of the crystalline semiconductor, direct and indirect. Both involve the interaction of an electromagnetic wave with an electron in the valence band, which is rose across the fundamental gap in the conduction band. The absorption coefficient α for direct transition is given by the relation

$$\alpha = \alpha_0 \frac{(h\nu - E_g)^n}{h\nu}$$

where E_g is the separation between bottom of the conduction and top of the valence band, hν is the photon energy, n is constant and is equal to 1/2 or 3/2 depending on whether transition is allowed or forbidden and α_o is a constant depending upon the transition probability for direct transition. For allowed direct transitions n =1/2 and for allowed indirect transition n = 2. Thus if the plot of $(\alpha h\nu)^2$ against hν is linear then the transition is direct allowed. The band gap energy Eg is determined by extrapolating the linear portion of the curve to the energy axis at 0.

Figure 3 below shows the UV-VIS absorption spectra recorded in the wavelength 300 nm to 800 nm at the room temperature. From the graph it is observed that the optical absorption increases suddenly at around 356 nm. The observed band gap energy value of ZnO nanorod is 3.4 eV. The observed band gap of nanocrystalline ZnO is well matching with previous reported values [11]

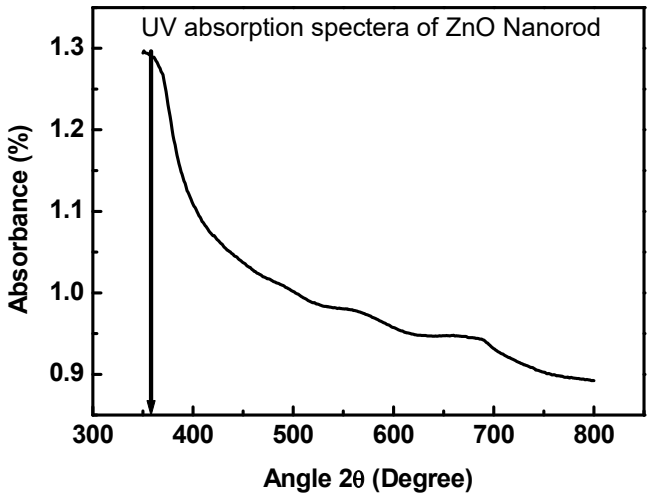

Figure 3: UV-VIS absorption spectra for the ZnO nanorad structure

Conclusions:

In the present work, the synthesis of ZnO nanorods by simple hydrothremal method was successfully performed. The structural and optical properties of the as-prepared ZnO nanorods have been confirmed using XRD, SEM and UV-VIS spectroscopy. According to Scherer's formula, the average particle size of the sample is 81 nm. Band gap energy of ZnO nanorod is 3.4 eV, obtained from the UV-VIS absorption spectra, which is higher than that of the bulk. Absorption peak of the prepared sample is 356 nm which is blue shifted as compared to the bulk (360 nm). Large band gap energy and blue shifted absorption edge confirm that the prepared ZnO nanorods exhibit strong quantum confinement effect.

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