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Structural And Optical Properties Of Spherical Shaped Wurtzite ZnS Nanoparticles In PVA Matrix

D. C. Deka*
S. Bordaloi and **U. Baishya**
Department of Instrumentation & USIC,
Gauhati University, Guwahati 781014
and S. B. M. S. College, Sualkuchi 781103, Assam, India

Abstract:

Nanocrystalline ZnS-PVA composite thin film is deposited on glass substrate by means of chemical method. The structural and morphological studies are carried out using XRD and TEM. The X-ray diffractogram of the sample shows wurtzite structure with preferred orientations along (002), (110) and (112) planes. The crystallite size is found be 3.54 nm. TEM micrograph of the film reveals the formation of spherical ZnS nano particles. The bandgap of the synthesized material is calculated using UV- Visible spectral analysis and bandgap plot. The bandgap value is found to be 3.8eV. Also we have used photoluminescence study to identify the defects in the nanostructure.

1. Introduction:

Nanomaterials are studied extensively because they show very different properties compared to what they exhibit in bulk form [1-3]. For example, as the size of the system decreases, the quantum size effect becomes pronounced where the electronic properties of the solid are altered. Meanwhile, the increase of surface to volume ratio changes the mechanical, thermal and catalytic properties of the material significantly. The distinct properties enable unique applications of nanomaterials. As an important II-VI group semiconductor material, ZnS has been intensively studied because of its wide application in optical sensor, photo catalysts in environmental protection, light emitting diodes, electroluminescence devices, photovoltaic devices, lasers, single electron transistors as well as biological sciences and diagnostics [4-13]. ZnS has wide bandgap of 3.68eV at room temperature. This bandgap can be

enhanced by decreasing the sizes of the crystallites.

In the present study, we report the successful synthesis of ZnS spherical nanoparticles in the polyvinyl alcohol (PVA) solution by chemical method. PVA is a hydrophilic polymer frequently used as a matrix for stabilization of ZnS nanocrystals extensively [14, 15].

2. Experimental details:

Nanocrystalline ZnS-PVA composite thin films are deposited on glass substrate by chemical route at 90^0C. The synthesis is carried out as follows- $1.33x10^{-5}$ mol PVA is stirred in 75 ml distilled water for 1.5hr with temperature controlled magnetic stirrer. Then the PVA solution is kept at rest for 2 hrs. A solution of 0.005mol zinc acetate in 5 ml NH_4 (OH) is mixed to the PVA solution. Lastly, a solution prepared by taking 0.015ml Na_2S in 25 ml distilled water is added to the above solution. Then the resulting mixture is heated to the temperature 90^0C and kept steadily at that temperature for 20 minutes. The solution containing ZnS-PVA is cast over glass slides to produce thin film form. After deposition of the films, the films are dried in vacuam and set for various characterizations. Structural characterizations of the films are determined by Philips X'pert prodiffractometer (PW-1830) at room temperature with CuK_α (1.54A°) radiation. Morphological studies are carried out using Transmission Electron Microscopy (JEM 100CXII JEOL, Japan). Optical transmission spectrum of the film is taken with the help of a UV Spectrometer (Hitachi U-3210 Spectrometer). Photoluminescence spectrum is recorded by Hitachi F-2500 Fluorescence Spectrometer.

3. Results and Discussions:

3.1 XRD Study:

Fig. 1 shows the X-ray diffractogram of the ZnS-PVA composite film. X-ray diffractogram of the film shown in fig. 1 exhibit broadened diffraction profile confirming formation of ZnS nanocrystals.

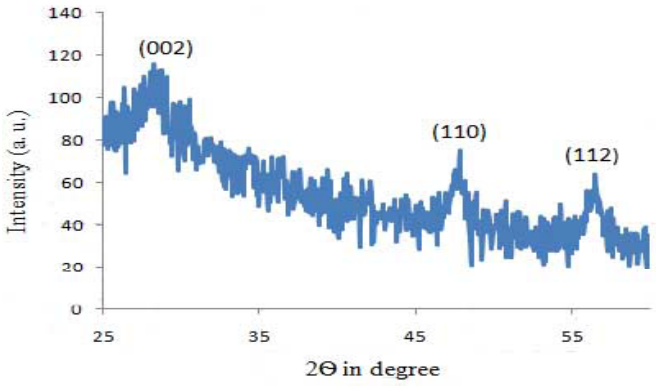

Fig.1 XRD spectrum of ZnS nanoparticles

The analysis of the profile shows preferred orientations along (002), (110) and (112) planes. The crystallite size (D) of the Nanocrystalline film is estimated by using Debye-Scherrer formula

$$D=0.89\lambda/\beta\cos\theta \quad (1)$$

Where λ, β and θ are the wavelength of the CuK_{α} radiation (1.54A°), full width at half maximum of the diffraction peak and diffraction angle respectively. The average crystallite size of the synthesized ZnS nanoparticles is found to be 3.54 nm.

3.2 TEM Study:

Fig. 2 shows the surface morphology of ZnS thin film deposited at 90^0 C. From the micrograph, it is observed that in the film the distribution of grains are not uniform throughout all the regions, but the film is without any void, pinhole or cracks and the grains cover the substrate surface well. We have clearly observed the nanosized spherical grains. The average grain size is found to be 6.10nm.

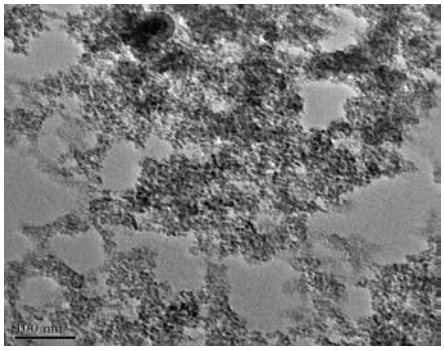

Fig.2 TEM micrograph of the synthesized ZnS nanoparticles

3.3 Optical Absorption Study:

Optical studies are carried out by measuring transmittance of the ZnS-PVA composite film deposited on glass substrate. Fig. 3(a) shows the transmittance (T) versus wavelength (λ) spectra of the as deposited film.

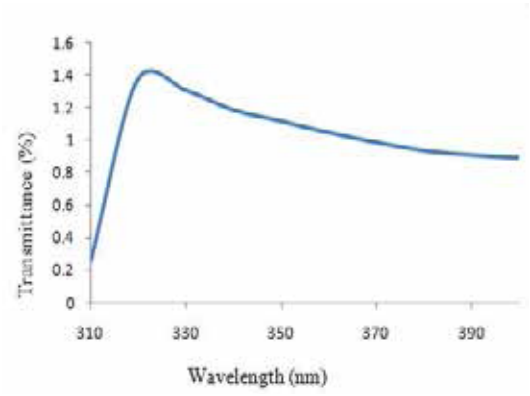

Fig. 3(a) UV-Visible transmission spectrum

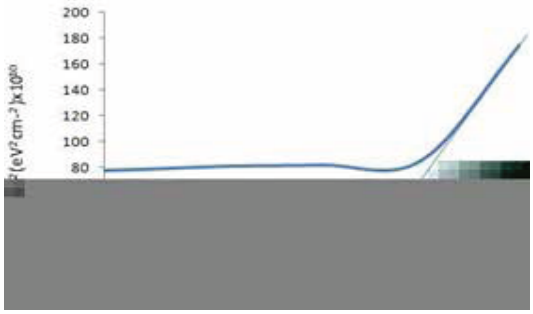

Fig. 3(b) Taue plot of ZnS nanoparticles

The relation between absorption coefficient (α) and incident photon energy (hυ) can be written as [16]

$$a = A\,(hn-E_g)^n / hn \quad (2)$$

where A is a constant, Eg is the band gap of the material and the exponent n depends on the type of transition. The

values of n for direct allowed, indirect allowed, direct forbidden transition are n = ½, 2 and 3/2 respectively. Graph between (hυ) versus $(\alpha h\upsilon)^2$ is plotted for the film is shown in fig. 3 (b) and the intercepts of the extrapolated straight line at $(\alpha h\upsilon)^2 = 0$ gives the direct band gap Eg of the material. The value of Eg is obtained as 3.80eV. It is observed that the bandgap value is higher than the bulk ZnS (3.6eV) which is due to the quantum confinement effect.

3.4 Photoluminescence:

PL spectrum measured at room temperature (290K) of the nanocrystalline ZnS-PVA composite film is shown in fig. 4. The sample is excited at 260nm. We have observed a weak peak centered 440nm and strong peak centered at 510nm. The weak peak, in more or less blue region of the spectrum is due to defect related emission of ZnS with short life time and the strong peak may be attributed to the stoichiometric defects, which might be a vacancy or an interstitial states.

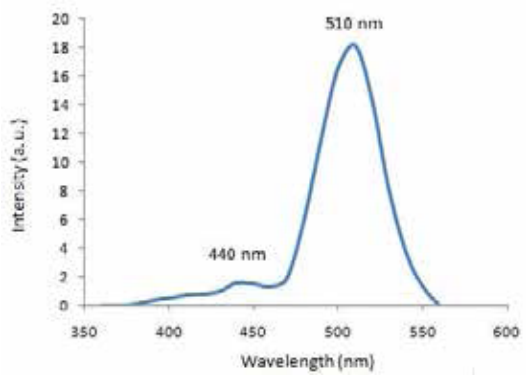

Fig. 4 Photoluminescence Spectrum of ZnS nanoparticles

4. Conclusion:

Spherical ZnS nanoparticles have been successfully synthesized by means of chemical method. The as-synthesized ZnS spherical nano particles have a wurtzite structure. The bandgap for direct optical transition of the synthesized ZnS nanoparticles is found to be 3.80 eV which is greater than its bulk value. These nanoparticles with green emission represent good candidates for use in optoelectronic devices.

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