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Optical Studies on Some Aspects of Polyvinyl Alcohol Composite Zns Nanocrystalline Thin Films

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Abstract

Zinc Sulfide (ZnS) nanoparticles were grown into the polyvinyl alcohol (PVA) matrix and were synthesized at 70^0C by chemical route. The particle size and surface morphology were analysed by X-ray diffraction (XRD), High Resolution Transmission Electron Microscopy (HRTEM) and Scanning Electron Microscopy (SEM). Optical absorption spectrum showed strong blue shift, which is an indication of strong quantum confinement. Photoluminescence spectrum shows the blue luminescence peaks, which can be attributed to the recombination of the defect states.

Keywords: Zinc Sulfide, Nanoparticle, Blue shift, Luminescence.

Introduction

Zinc sulfide (ZnS) is a direct transition semiconductor with the widest energy band gap (3.68 eV) among the II-VI compound materials. The most striking feature of ZnS nanocrystallites are that their chemical and physical properties differ dramatically from those of bulk solids [1-3]. Semiconductor nanoparticles exhibit size dependent electronic band gap energies [4]. In addition to this doped semiconductor nanoparticles have tremendous potential for use in light emitting applications. ZnS nanoparticles can be obtained by different techniques, such as screen printing [5], electro deposition [6], molecular beam epitaxy (MBE) [7], physical vapour deposition [8] etc. Among them chemical deposition is one of the most promising techniques for thin film synthesis since it allows for a continuous coverage of rough surfaces with a minimum thicknesses at low cost. Keeping all these aspects in view, we have carried out a systematic study on the optical properties of ZnS nanoparticles in the regime of strong confinement by chemical process [9]. In the present study we report the chemical deposition of ZnS nanoparticles and their characterization by X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), UV-VIS spectrometry and PL spectrometry.

Experimental Method

ZnS nanoparticles were synthesized using polyvinyl alcohol (PVA) as a matrix. PVA being a good solute to multiple phase system, it provides uniform gaps that are very close to each other and distributes in the form of array. 2 wt% solutions of PVA was mixed with $ZnCl_2$ under a high stirring rate (200rpm) condition using magnetic stirrer. The constant temperature 70^0 C for 3 hours was maintained during the process of stirring. The sample under preparation was kept for 12 hours for complete dissolution to get a transparent solution. An equimolar solution of Na_2S was added drop by drop to this solution, until it appears completely milky. The ZnS nanoparticles containing PVA were cast over properly cleaned glass substrate to produce thin film form. The chemical reaction occurs as follows

$$ZnCl_2 + Na_2S \longrightarrow ZnS + 2NaCl$$

Results and discussion

XRD Measurements

The XRD pattern of the prepared sample was taken by Seifert XRD (3003TT) operating at 40KV-30mA. Figure 1 shows the XRD pattern of ZnS thin film. The three broad peaks observed in the diffractogram can be assigned to the planes (111), (220) and (311) respectively [10]. The peak broadening in the XRD patterns clearly indicates the formation of ZnS nanocrystal of small size.

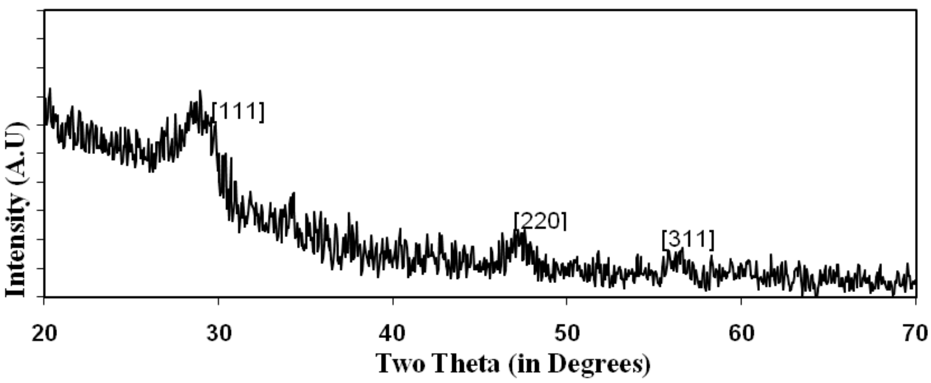

Figure 1: XRD patterns of ZnS Thin films.

From X-ray diffraction study, average particle size has been calculated by using Debye Scherrer formula [11].

$$D = K\lambda/\beta_{2\theta}\cos\theta.$$

where θ is the Bragg angle, $\beta_{2\theta}$ is the full width half maxima, λ is the X-ray wavelength and K=0.89 [12]. The calculated size is found to be 4 nm.

Optical Absorption

The absorption spectrum of the ZnS sample shown in FIGURE 2was measured using a HITACHI-U 3210 UV-VIS spectrometer.

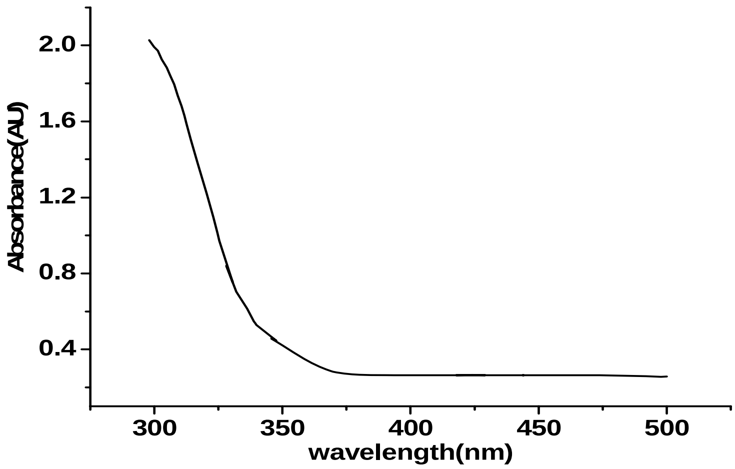

Figure 2: Absorption spectra of ZnS nanoparticles.

It is clear from figure 2 that the sample exhibit absorption at wavelength suggesting blue shift w.r.t. the bulk arising from quantum confinement effect in the nanoparticles. The band gap of the sample was determined using the relation,

$$(\alpha h\upsilon) = C\,(h\upsilon - Eg)^{1/2}$$

where C is a constant, Eg is the band gap of the material. The value of the optical band gap is calculated by extra plotting the straight line portion of $(\alpha h\upsilon)^2$ vs. $h\upsilon$ graph (figure 3) to $h\upsilon$ axis. The obtained band gap value of the sample is 3.96 eV which is blue shifted as compared to the bulk band gap value.

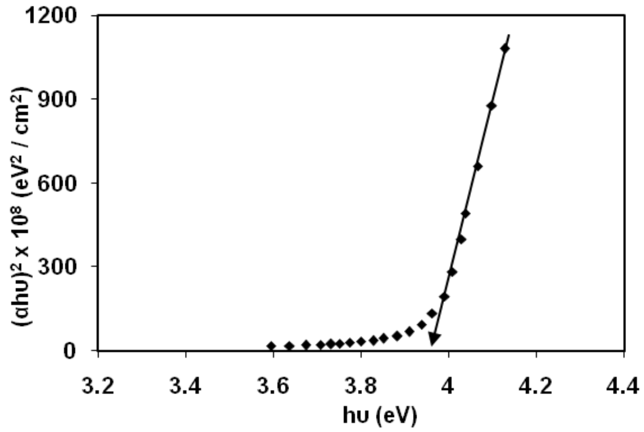

Figure 3: Band gap determination of ZnS nanoparticles.

Photoluminescence (PL)

The photoluminescence spectrum measured at room temperature of ZnS nanocrystalline thin film deposited on glass substrate as shown in figure 4. The spectrum was recorded using (F 2500) FL spectrometer.

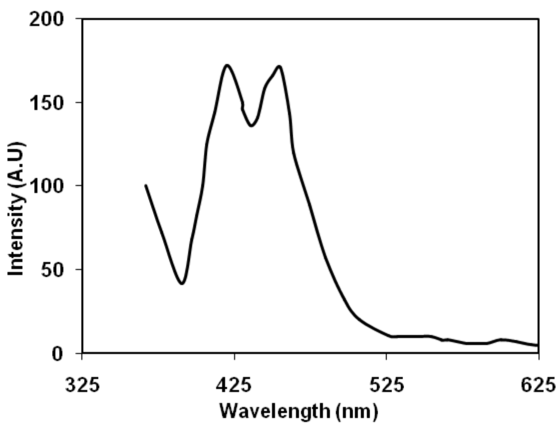

Figure 4: PL spectra of ZnS nanoparticles.

In figure 4 the two peaks positioned are around 415 nm and 440 nm. The blue emission at 415nm is attributed to sulphur vacancies[13] and the emission peak at 440 nm is attributed to the zinc vacancies which is quite agree as reported by other workers [14, 15].

Scanning Electron Microscopy (SEM)

Surface morphological study of the ZnS thin film was done using the scanning electron microscope (HITACHI S-530).

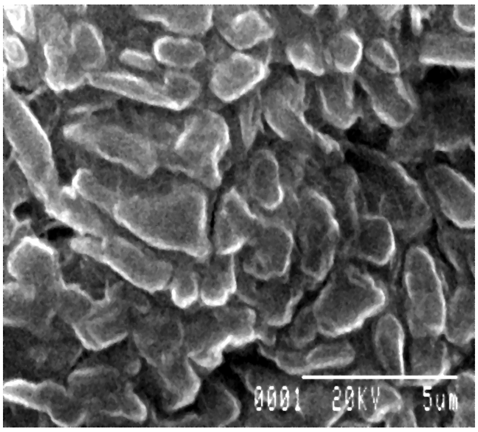

Figure 5: SEM image of ZnS nanoparticles.

Figure 5 shows that the "as-deposited" film is not uniform throughout all regions but the films are without any void, pin hole or cracks and that they cover the substrate well, making them suitable for device applications.

Transmission Electron Microscopy (TEM)
Transmission electron microscopy (TEM) image was obtained using a JEOL JEM 2100 electron microscope operated at 200 KV.

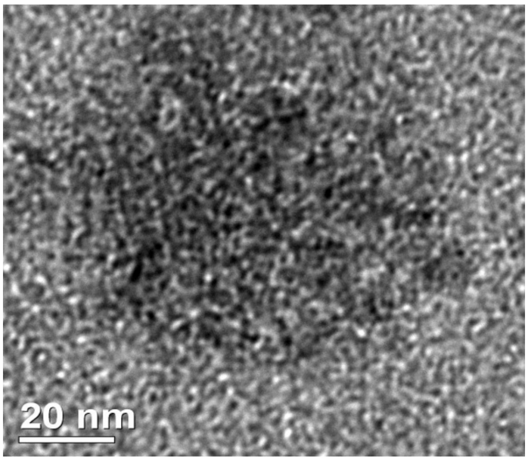

Figure 6: TEM image of ZnS nanoparticles.

HRTEM image of the ZnS sample shown in figure 6 indicates the nanocrystalline nature of the sample with distinct grain boundaries having average crystallite size of 3.8 nm. The nanoparticles have also seen to be of more or less spherical shape with clear lattice fringes showing the well crystallized particles. The size is also nearly consistent with the size obtained from XRD observations.

Conclusion

Zinc sulphide (ZnS) nanoparticles are prepared by chemical methods. The XRD measurement yielded the particle size around 4 nm which is quite agree with the HRTEM result. The optical band gap energy of the sample is found to be 3.96 eV which exhibit strong quantum confinement effect. Room temperature photoluminescence (PL) of the sample exhibit a blue emission peaked at 440 nm.

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