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OPTICAL AND PHOTOLUMINESCENCE STUDIES OF VACUUM EVAPORATED ZnSTHIN FILMS

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Thin films of ZnS of different thickness have been prepared on glass substrates at room temperature by vacuum deposition. The thickness of the deposited films was measured by employing quartz crystal monitor method. The optical properties have been studied in the range of wavelength 250-500nm. The optical band gap, absorption coefficient and extinction coefficient values of different thickness have been estimated. The Photoluminescence emission spectra of ZnS films of thickness 550Å, 1150Å and 1850Å have been studied with different excitation wave lengths. In Photoluminescence spectra, recombination processes are observed with emission energies less than E_g. The intensity of the PL signal at the room temperature, averaging of the experimental points can be carried out in order to find more clear PL characteristics.

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1. Introduction

The ever widening search for new thin films materials to meet the challenging demand, which has lead to the selection of inorganic material [1-2]. Because of these, semiconductors are becoming very popular due to their wide band gap engineering [3-5]. Zinc Sulphideis an important semiconductor with the band gap energy Eg = 3.24eV. The semiconducting ZnS possess unique electronic properties, which are essential in device fabrication like photo diodes, solar cells, photo detectors, light emitting device and thin film resistors [6-8]. Among various methods the reliable, simple and cost effective route to synthesis ZnS thin film is vacuum evaporation techniques and also the development of low cost solar cells depends on the exploitation of the thin films and thus ZnS films obtained various experimental conditions require comprehensive optical characterization [9-11]. Zinc Sulphidebelongs to II – VI group of a semiconducting material and they have higher band gap energy than the corresponding III – V compounds due to the larger iconicity in II – VI compounds [12-14]. Also, the effective mass of mass carriers in II – VI compounds is relatively high, the radiative carries life time is small and the carrier diffusion length is short as compared with the III – V compounds. The optical absorption spectrum showed an exponential edge. Standard Photoluminescence (PL) spectroscopy is a sensitive, non-contact and non-destructive tool such as substitutional impurities (donors, acceptors) and native or intrinsic defects in ZnS thin films [15-17]. A PL emission spectrum provides information concerning the point defect nature of the crystal and thin film. By focusing the exciting laser light to a small spot, PL mapping can be used as a sensitive probe of lateral variations in structural quality, impurity concentrations and stoichiometry and hence in measuring the homogeneity of composition and doping.

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2. Experimental details

The ZnS powder of purity 99% was evaporated using Tungsten conical basket (200 amps) under the pressure of 2 x 10^{-5}Torr on to a pre cleaned glass substrate (3.25 x 2.75 x 0.1 cm dimension). The pressure was obtained by diffusion pump backed by rotary pump in the coating unit and was measured using Pirani and Penning gauge. A constant rate of evaporation of the order of 1 Å / sec was maintained throughout the film fabrication. A rotary device was employed to maintain uniformity in film thickness. The thickness of the film was controlled and measured by Quartz crystal monitor and the thickness monitor in a flat circular plate approximately 0.05 inch (1.4cm) in diameter and 0.011 inch (0.28 cm) thick. A substrate heater arrangement was employed to grow the thin film at different substrate temperature. The Copper-constant and thermocouple was employed to measure the temperature inside the chamber. The optical transmission measurements were made in the spectrum range (190 – 2500mm) through UV-visible spectrometer [JASCO CORP V570] using unpolarized light at near normal incidence. Double beam spectrometers were used in all ranges [18-19]. The optical constants have been evaluated form the measured values of the transmittance and the wavelength of light.Photoluminescence characterization was carried out by Fluoromax-4 spectrometer in which Xenon is used as source.

2. Result and Discussion

2.1 Optical Properties

Transmission spectra of films were recorded as a function of wavelength in the range of 250-500nm. The transmittance spectra of the ZnS films in the visible region for the different thickness films are shown in the Fig.1. It reveals that the transmittance decreases with the increase of film thickness.

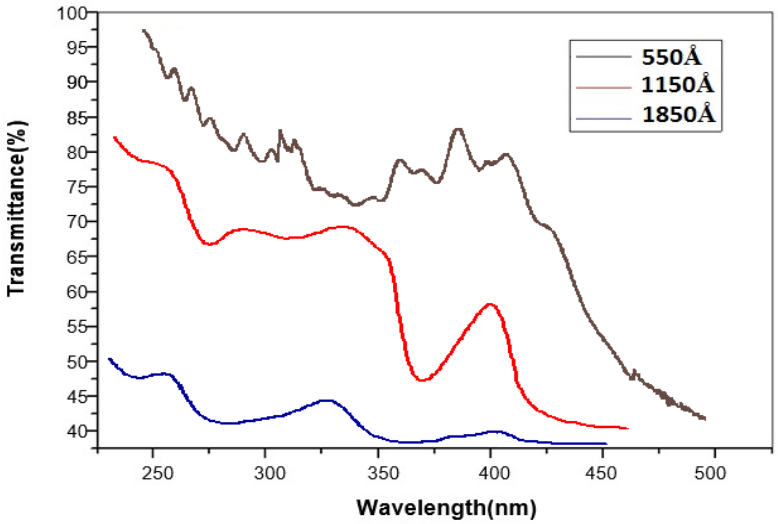

Fig. 1. Transmittance Spectra of ZnS thin films for various thickness

From the Fig.2. Optical properties of ZnS thin films are determined from absorbance measurements in the range of 250-500nm. The absorption coefficient can be written in terms of the incident radiation energy.

$$\alpha = A\,(h\gamma - Eg) \qquad (1)$$

Where ‘h’ is the Planck’s constant and ‘γ’ is the frequency of the incident radiation.

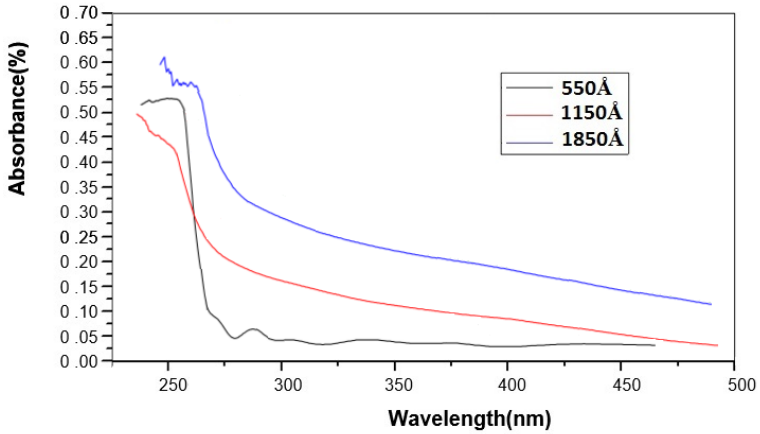

Fig. 2.Absorbance Spectra of ZnS thin films for various thickness

From the Fig. 3.the value of Extinction Coefficient (K_f) decreases with the increases in the film thickness. Absorption coefficient (α) associated with the strong absorption region of the films was calculated from absorbance (A) and the film thickness (t) using the relation.

$$A = 2.3026\ A/t \tag{2}$$

The Extinction coefficients are calculated using the equation.

$$K_f = 2.303\ \lambda \log (1/T_0) / 4\pi d \tag{3}$$

The extinction coefficient (K_f) is directly related to the absorption of light. In the case of polycrystalline films, extra absorption of light occurs at the grain boundaries. This leads to non-zero value of (K) for photon energies smaller than the fundamental absorption edge.

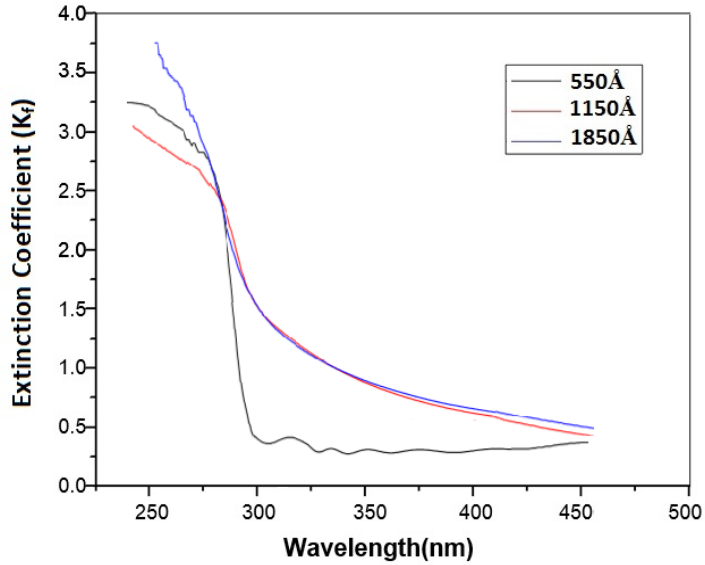

Fig. 3. Thickness dependence of Extinction Coefficient (K_f)

The optical band gab can be obtained by extra plotting the linear portion of the plot $(\alpha h\gamma)^2$Versus hγ. From the plot, the variation of $(\alpha h\gamma)^2$ Versus photon energy for different thickness (550 Å, 1150 Å, 1850 Å) ZnS thin films are shown in Fig. 4. The presence of a single

slope in the curves suggests that from thermal evaporation are of single phase in nature and the type of transition is direct and allowed.

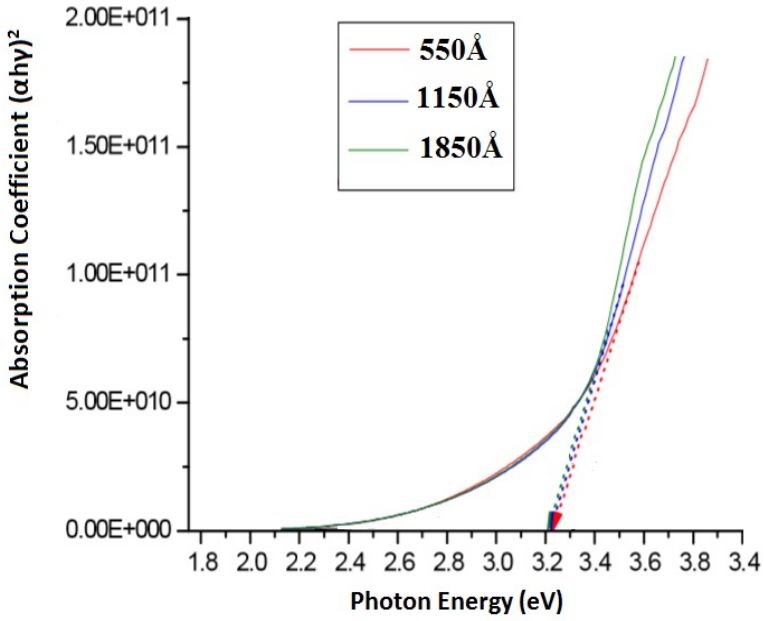

*Fig. 4. A plot of $(\alpha h\gamma)^2$ Vs. (hν) for ZnS thin film of thickness*550 Å, 1150 Å &1850 Å

From these absorption peaks, the direct and allowed band gap energy is evaluated from the plot $(\alpha h\gamma)^2$Versus hγ are shown in table 1.

Table 1. Variation of energy gap, Absorption coefficient and Extrinsic coefficient with thickness.

Thickness Å	Band gap energy (eV)	Absorption coefficient	Extrinsic coefficient
550	3.24	2.13	0.91
1150	3.18	2.97	0.73
1850	3.12	3.47	0.60

The observed decrease in the band gap energy with increases in thickness is due to the changes in the barrier height to the size of the grain in crystalline film and large density of dislocation.

2.2 Photoluminescence studies

The Photoluminescence emission spectra of ZnS films of thickness 550Å, 1150Å and 1850Å have been studied with different excitation wave lengths. Photoluminescence signals at room temperature for the ZnS film of thickness 550Å by vacuum evaporation technique is shown in Fig. 5. The excitation wavelength 350nm (3.74 eV).The spectra shown in Fig. 6.exhibit high energy band at 3.28 eV and the low energy bands appear around 3.14 eV for the samples with thickness d = 1150Å and d = 1850Å respectively. A shift in low energy band at 2.72 eV has been noticed for the sample of thickness d = 550Å. However, for thickness d = 1850Å sample exhibits two energy bands with low intensity around 2.86 eV and another one at 3.10 eV. Further a high energy broad band with a maximum at 4.20 eV appear for all the samples with d = 550Å, 1150Å and 1850Å respectively.

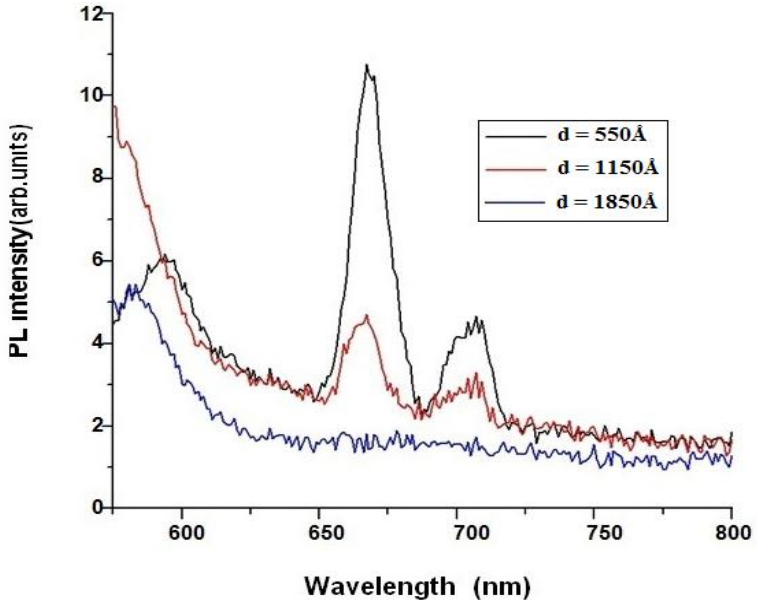

Fig. 5. Photoluminescence spectra of ZnS films of different thickness excited with 350 nm

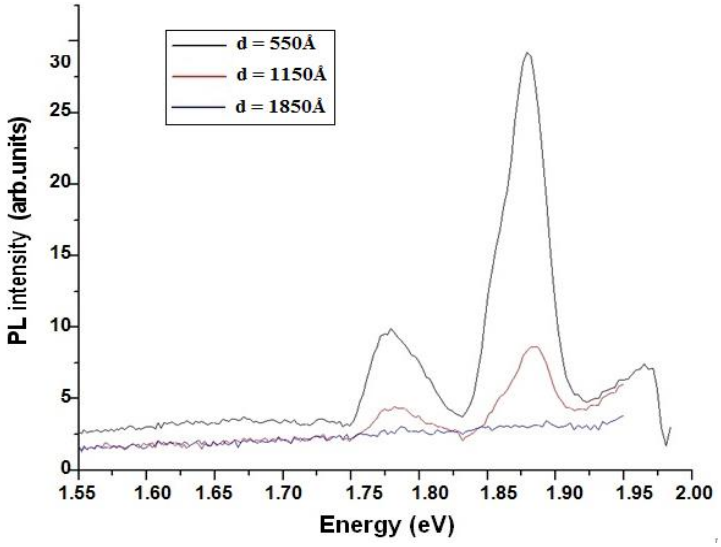

Fig. 6. Photoluminescence energy band spectra of ZnS films of different thickness excited with 350 nm.

The green emission bands corresponding to 3.28 eV are attributed to the transition of sulfur vacancy (V_S) to the valence band and the donor acceptor pair recombination. Since the energy separation between green band (3.28 eV) and the band to band transition (3.42 eV at room temperature) is approximately 2.72 eV, this probably excludes the possibility of the recombination of free electron with holes localized at V_{Zn} and I_S. The red emission band centred at ≈2.46 eV, but the trend is similar to that of the green emission band. The red emission band has been ascribed to surface states in particular Zn-vacancies.

Fig. 7.shows the PL emission spectra for the ZnS samples excited with 450 nm (3.82 eV). In Fig. 8, the spectrum exhibits the low energy bands around 2.72 eV and 3.28 eV for the sample with d = 1850Å and d = 1150Å respectively. High energy bands with low intensities centred around 3.12 eV, 3.18 eV and 3.24 eV are also noticed for d = 550Å, 1150Å and 1850Å respectively. Thick samples exhibit PL around 3.12 eV refers to the green emission band whereas 3.18–3.24 eV range indicates the blue signal.

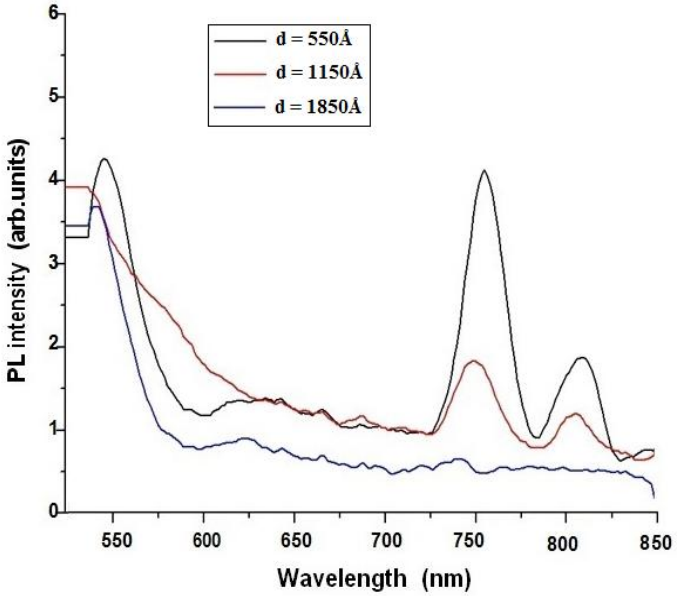

Fig. 7. Photoluminescence spectra of ZnS films of different thickness excited with 450 nm.

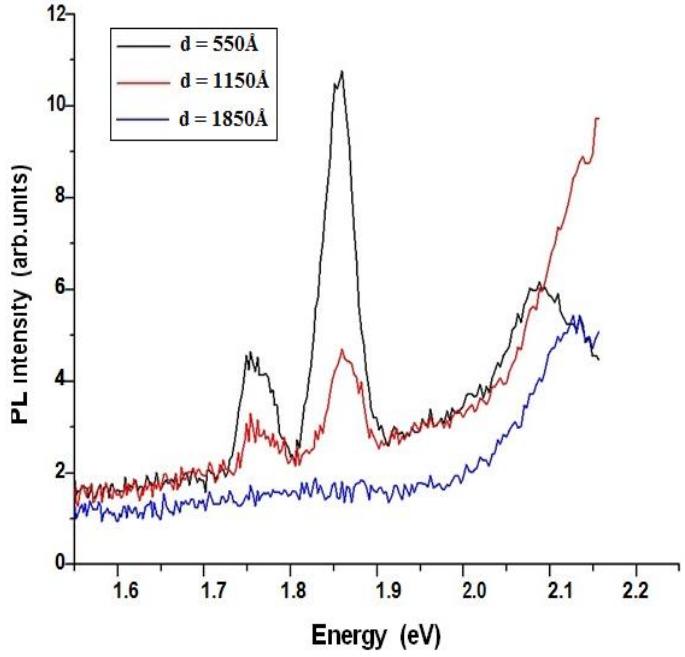

Fig. 8. Photoluminescence energy band spectra of ZnS films of different thickness excited with 450 nm.

PL signals at room temperature for the as-grown ZnS films by vacuum evaporation technique excited with 500 nm (2.70 eV) are shown in Fig. 9. The spectrum exhibits a high energy broad band centred on 4.92 eV whereas the low energy bands appear around 2.28eV and 2.42 eV for the sample with d = 1850Å which is shown in Fig. 10. Similar broad bands are noticed at 3.14 eV, whereas the low energy bands appeared around 2.46 eV and 2.58 eV for d = 550Å & 1150Å respectively with varying intensities.

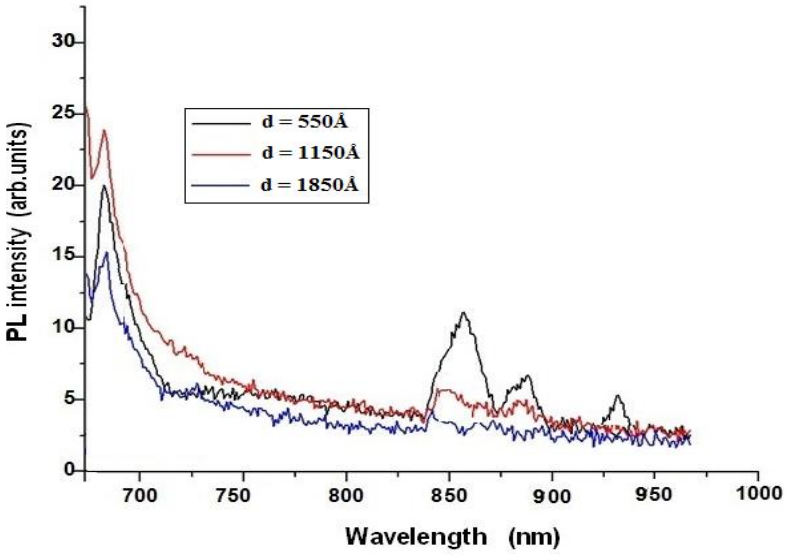

Fig. 9. Photoluminescence spectra of ZnS films of different thickness excited with 500 nm.

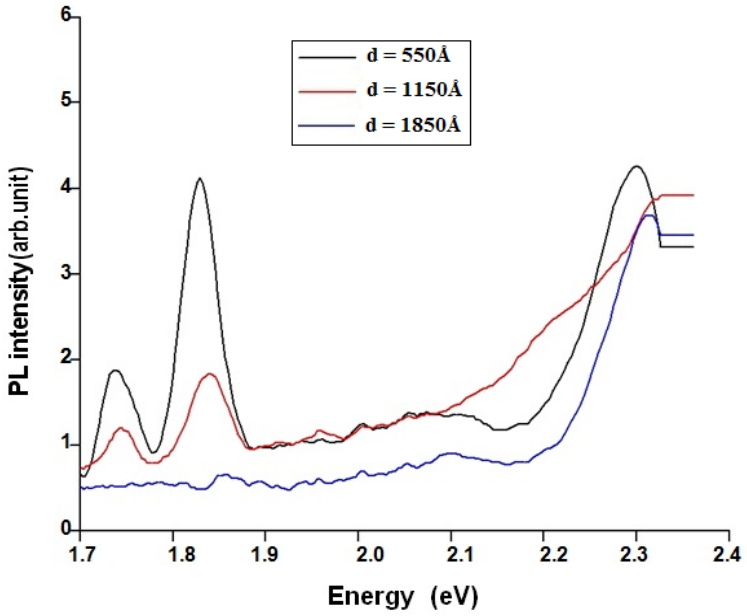

Fig. 10. Photoluminescence energy band spectra of ZnS films of different thickness excited with 500 nm.

The higher energy band in the Green region (3.42 eV) is related to near band edge emission recombination and the low energy feature is related to deep level transitions, which accounts reasonably a good crystalline quality of the samples. Due to the low intensity of the PL signal at the room temperature, averaging of the experimental points can be carried out in order to find more clear PL characteristics.

3. Conclusions

ZnS thin films grown on glass substrates using High Vacuum Evaporation method. The transmittance and absorbance spectra in the range of 250-500nm has been taken by using FTIR spectrometer. In absorbance spectra, the material has a high absorbing nature. The observed band

gap energy and extinction coefficient has inversely dependent on film thickness. The absorption coefficient increases as the thickness of the material increases. The prepared ZnS may have future applications in nanoscale optics, electronics and magnetic. From photoluminescence studies, it is clear that ZnS films are photosensitive. Therefore, they find applications in photoconductor and fluorescent materials with Green and Red band Emissions.

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