

## **Characterization of ZnS Thin Film Synthesized by CBD using Zinc Acetate Precursor**

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### **ABSTRACT**

In the present work, ZnS thin film was grown on glass substrate chemical bath deposition (CBD) method at room temperature using zinc acetate as source of zinc ion. Characterization techniques of XRD, SEM, FESEM, TEM and EDX were utilized to study the microstructure of the films. Microstructure consists of many spherical shaped particle well covering the substrate surface. EDX confirmed formation of nearly stoichiometric film. Particle size estimated from X-ray line broadening analysis using Scherrer equation was ~ 15 nm which is also confirmed by TEM picture. The value of the energy gap of ~ 3.85 eV is on the higher side of the bulk value indicating quantum confinement arising from particle size lowering.

**Keywords:** ZnS thin film, CBD, particle size, microstructure, band gap

### **1. Introduction**

Recent investigations have evoked considerable interest in ZnS thin films due to their vast potential for use in thin film devices such as photoluminescent and electroluminescent devices and more recently as *n*-type window layer heterojunction solar cells [1-3]. Zinc sulphide (ZnS) is an important II-VI semiconducting material with a wide direct band gap of ~3.70 eV in the bulk that is enough to emit visible light without absorption and the efficient transport of high energy electrons. Thus it can render more transparency in the short wavelength region between 350 and 550 nm in comparison with the CdS with band gap energy of 2.42 eV [4]. The material crystallizes in both cubic and hexagonal forms and is a material of reference to test several theoretical models in condensed matter physics [5-6]. Also, the high refractive index of ZnS (*n*~2.4) allows it to be used as an antireflective coating or to be combined with a high refractive index material [4, 7]. Zinc sulfide has found wide use as a thin film coating in the optical and microelectronic industries [5]. Various physical and chemical techniques have been employed to prepare thin films of ZnS. Vapor-phase deposition methods such as r.f. sputtering, metal organic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE) and atomic layer epitaxy (ALE) demand the use of either vacuum conditions and/or complex equipment. In contrast, chemical bath deposition (CBD), also known as chemical solution deposition, is a method that is simple,

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convenient and inexpensive. Films may be deposited at low temperatures on a variety of substrates. The thickness of the deposited layers may be readily controlled by variation of the deposition time. The process should be easily adaptable to large area processing with low fabrication cost. Thin films deposited by this method can be of high quality and studies of the deposition of ZnS by CBD. Although there are reports of room temperature synthesis of ZnS thin films by CBD [4-5], majority of researchers reported synthesis of ZnS at enhanced bath temperature [7-10]. Also primarily zinc sulphate and zinc chloride has been used as the source of zinc ion in most these works. In the present work, we present the chemical bath deposition of ZnS thin films using zinc acetate as source of zinc ion and characterization of the synthesized samples. Zinc acetate has a number of advantages compared to other zinc complexes. It is known to be a 'mono- precursor' [11]. Also the ammonium acetate formed during its reaction with ammonia is highly soluble in water which reduces the possibility of impurity incorporation in the deposited films. Ammonium acetate is also a relatively unusual example of a salt that melts at low temperatures. Although Ubale et al [5] used zinc acetate as precursor of zinc ion; they have reported detailed electrical characteristics of the films. In the present work, structural and morphological characterization of ZnS thin films synthesized by CBD using zinc acetate precursor is reported.

## 2. Experimental

ZnS thin film was deposited on properly cleaned microscope glass slide substrates. Prior to deposition, the substrates were ultrasonically cleaned with acetone followed by rinsing in isopropyl alcohol, and deionized water for 15 minutes, respectively. The glass substrates were mounted vertically in the reacting bath using a specially designed substrate holder. All the chemicals and reagents used to prepare the reacting bath were of analytical reagent grade. 80 ml 0.2 M zinc acetate  $[Zn(CH_3COO)_2 \cdot 2H_2O]$  and 160 ml 0.2 M thiourea  $[(NH_2)_2CS]$  was added and stirred properly at room temperature (30°C). Ammonia solution was added to make the bath pH 10.5. The well treated slide was immersed within the solution for three (3) days a white colored with a faint shadow of blue appears. XRD confirmed formation of ZnS.

The film thickness was measured using fiber optic spectrophotometer (Ocean Optics International, Model SD2000). Light beam from tungsten source at normal incidence was used to measure the reflectance. X-ray diffraction (XRD) with  $CuK_{\alpha}$  radiation ( $\lambda=1.5418 \text{ \AA}$ ) was performed to assess the overall structure and phase purity. The experimental peak positions were compared with the standard JCPDS files and the Miller indices were indexed to the peaks. Scanning electron microscopy (SEM, Model S530, Hitachi, Japan) was used to study the surface morphology and to illustrate the formation of crystallites on the film surface. Field emission scanning electron microscopy (FESEM) was used to measure the particle size. The same instrument was used for energy dispersive X-ray (EDX) analyses for qualitative analysis of the elements present. The Transmission electron microscopy (TEM) investigation was carried out using Tecnai F30 G<sup>2</sup>, FEI, Hillsboro, Oregon microscope operating at 200 kV. TEM was used for particle size estimation. The sample was detached from the substrate and dispersed in ethanol using ultrasonic bath, mounted on a carbon coated copper grid, dried, and used for TEM measurements. UV-VIS spectrophotometric measurements were performed

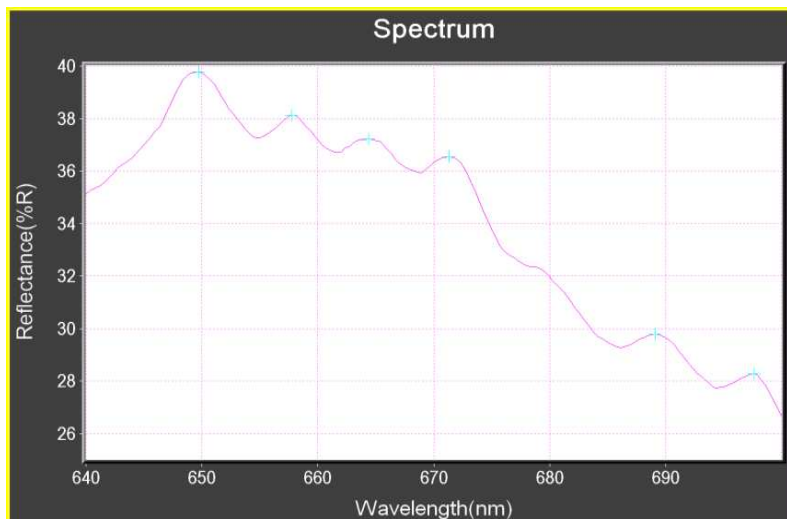
Characterization of ZnS thin film synthesized by CBD using zinc acetate precursor using a double beam spectrophotometer (Shimadzu, UV-1800) at room temperature. The spectra were recorded by using a similar glass as a reference and hence the absorption due to the film only was obtained. The band gap of the films was calculated from the absorption edge of the spectrum. The PL intensity is measured using a laboratory made arrangement with laser source.

### 3. Results and discussion

Figure 1 show the optical reflectance spectrum for ZnS thin film obtained from fiber optic spectrophotometer (Ocean optics, SD 2000). Figure shows the dependence of reflectance ( $R\%$ ) against incident photon wavelength ( $\lambda$ ). The film thickness ( $t$ ) was calculated using the relation

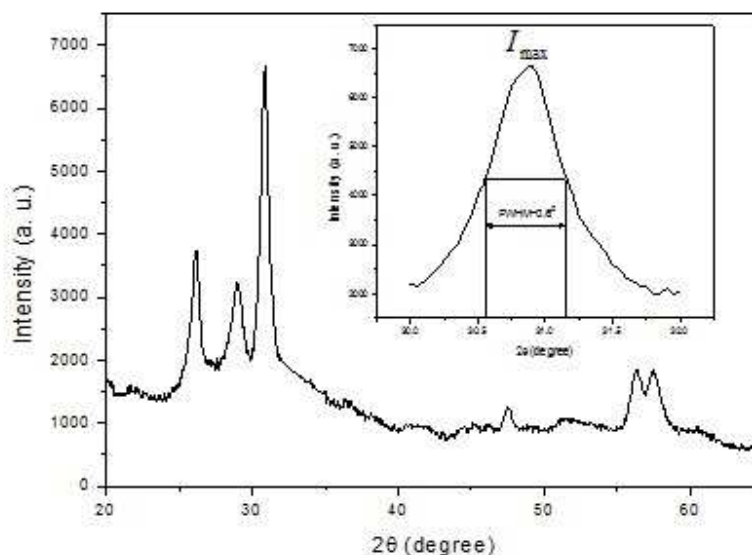
$$t = \frac{m}{2D\mu}$$

where  $m$  is the number of fringe,  $\mu$  is the refractive index of the material and  $D = \lambda_1^{-1} - \lambda_2^{-1}$ .  $\lambda_1$  and  $\lambda_2$  are the wavelengths of the  $n$  th and  $(n + m)$  th fringe. The maximum values correspond to bright fringes and minimum values correspond to dark fringes. The film thickness evaluated was  $\sim 1.3 \mu m$ .



**Figure 1:** Reflectance pattern of ZnS thin film

Figure 2 shows the XRD pattern of ZnS thin film in the scan range 20-70°. The major peaks at 26.2°, 28.95°, 30.86°, 47.5°, 56.35° and 57.45° can be well indexed to the hexagonal structure of ZnS [JCPDS file no. 36-1450]. The corresponding reflecting planes are (100), (002), (101), (112) and (201) respectively. Inset shows the major peak at 30.86° (expanded view).  $I_{\max}$  represents the maximum intensity.



**Figure 2:** XRD spectrum of *ZnS* film (Inset shows the major diffraction peak)

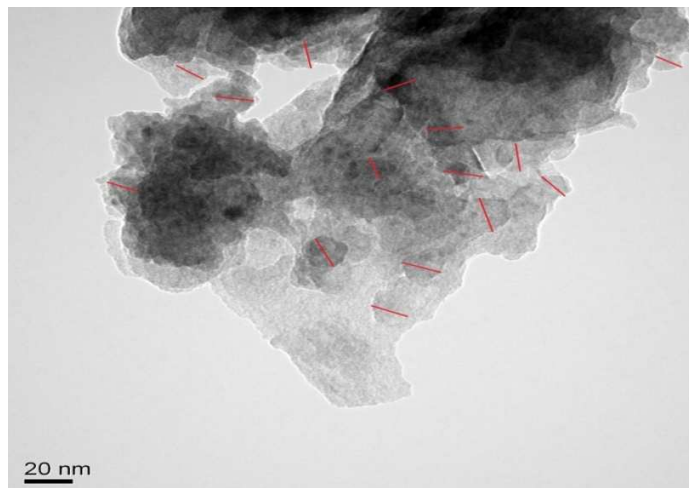
The value of full width at half maximum intensity (FWHM) of  $\sim 0.6$  was used to find the particle size using Scherrer equation [12-14]:

$$D = \frac{k\lambda}{\beta \cos \theta}$$

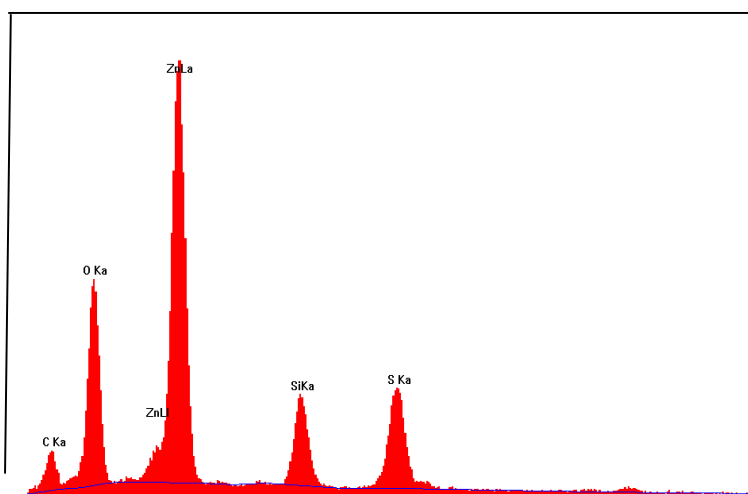
where  $\lambda$  is the wave length of radiation used ( $CuK_{\alpha}$ ,  $\lambda = 1.5418 \text{ \AA}$  in this case),  $k$  is the Scherrer constant ( $\cong 0.9$ ),  $\beta$  represents FWHM in radian,  $\theta$  is the diffraction angle of the concerned diffraction peak for which FWHM is evaluated and  $D$  is the Crystallite dimension (or particle size). The average particle size calculated using Scherrer formula is  $\sim 15$  nm.

Figure 3 shows the TEM image of *ZnS* nanoparticles. The particle size is measured using Image J software from the TEM image [15]. The calculated average particle size is  $\sim 14.3$  nm which matches well with value obtained from XRD data. Figure 4 shows the EDX spectra for *ZnS* film confirming the existence of *Zn* and *S* elements. The peaks appearing at 0.52 keV and at 1.72 keV are due to oxygen and silicon appears from the substrate component. Contamination of trace amount of carbon was detected in the film.

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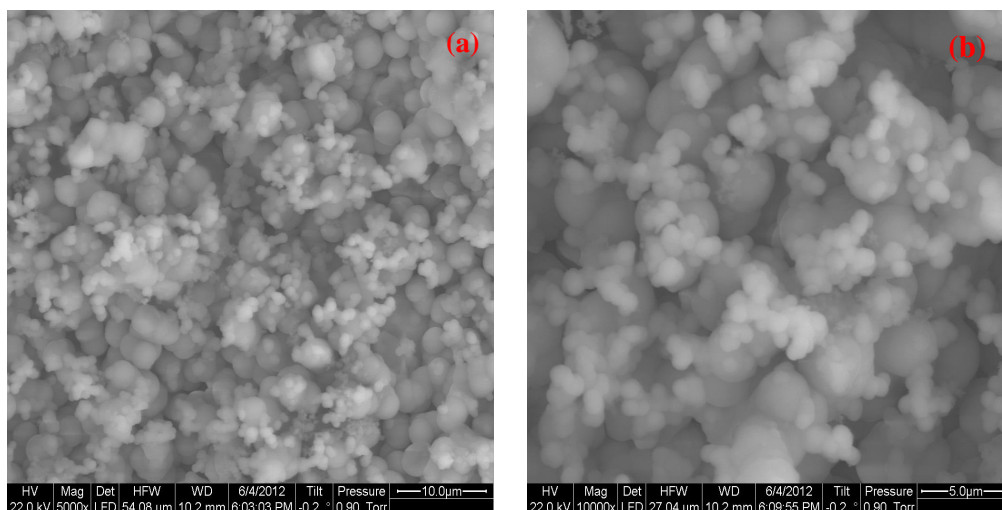


**Figure 3:** TEM image of ZnS

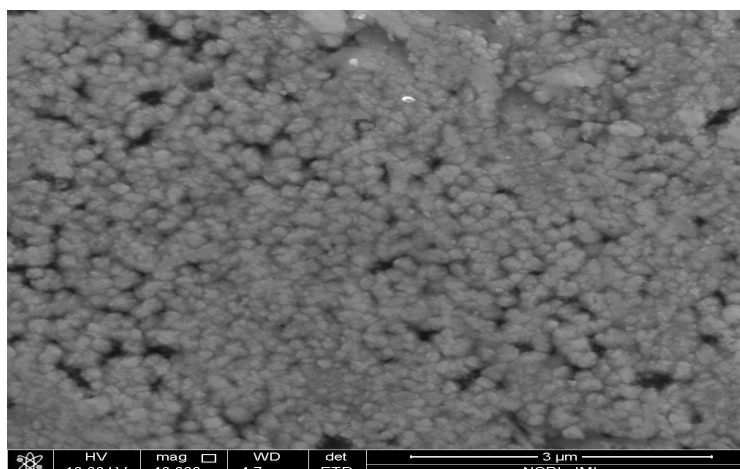


**Figure 4:** EDX spectrum of ZnS film

The microstructure of ZnS thin film is shown in figure 5 at different magnification. Figure 5 (a) shows SEM image at normal incidence with magnification  $\times 5000$ . The SEM photograph illustrates the formation of sub-micrometer crystallites well covering the substrate surface. Agglomeration of small crystallites seems to be present in certain regions on the film surface which is also visible in the SEM image with magnification  $\times 10000$  (Figure 5 (b)). Globular aggregates of microdimensions is clearly seen in figure 5 (b). Figure 6 shows the FESEM image of the film. It is evident that the microstructure consists of many off spherical shaped clearly defined grains covering the substrate surface more or less uniformly.



**Figure 5:** SEM image of  $ZnS$  (a) with magnification  $\times 5000$  and (b) with magnification  $\times 10000$



**Figure 6:** FESEM image of  $ZnS$

Optical band gap ( $\epsilon_g$ ) was determined from the dependence of absorption coefficient ( $\alpha$ ) on photon energy ( $h\nu$ ) using Tauc's formula for direct transition

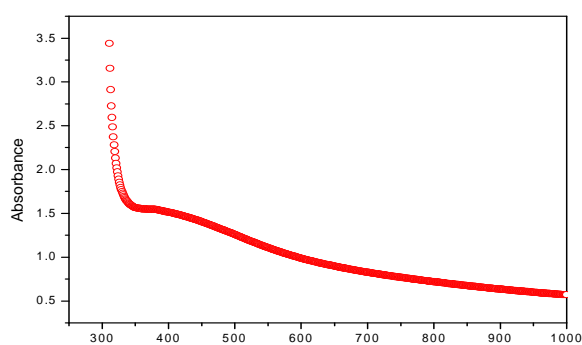
$$(\alpha h\nu)^2 = A(h\nu - \epsilon_g)$$

where  $\nu$  is the frequency,  $\alpha$  is the absorption coefficient,  $A$  is a function of index of refraction and hole/electron effective masses, and  $h$  is the Planck's constant [16-17]. The plot of  $(\alpha h\nu)^2$  against  $h\nu$  is shown in figure 7 (Inset shows the plot of absorbance against wavelength). Absorption coefficient ( $\alpha$ ) was evaluated from the relation



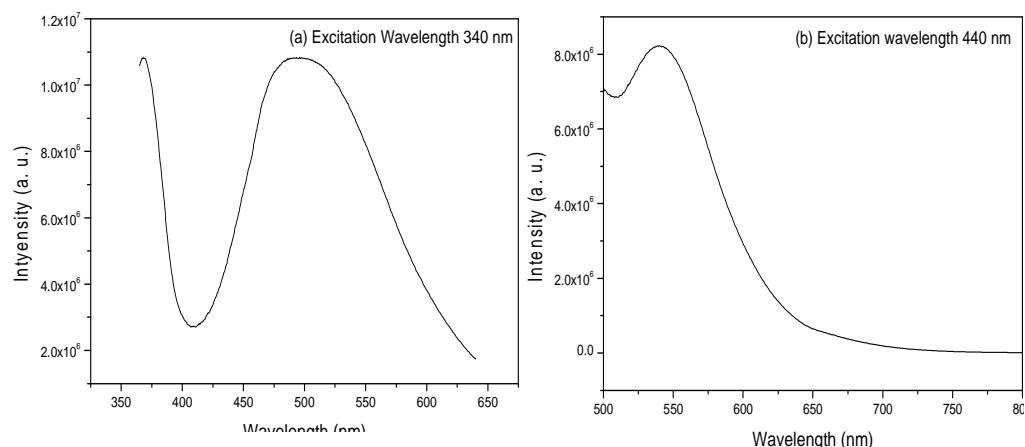
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$A = 2.303\alpha t$  and using a value of thickness  $\sim 1500$  nm measured using fiber optic spectrophotometer. The optical energy gap was obtained when the straight line portion of the  $(\alpha h\nu)^2$  vs.  $h\nu$  plot is extrapolated to intersect the energy axis at  $\alpha = 0$ . The direct band gap of ZnS deposited calculated is 3.851 eV, which is on the higher side of the bulk value and might be due to quantum confinement arising from particle size lowering.



**Figure 7:** Plot of  $(\alpha h\nu)^2$  vs  $h\nu$  (in eV) of ZnS

Figure 8 shows PL intensity spectrum of ZnS thin film. The sample is photoexcited at excitation wavelengths of 340 nm and 440 nm. The plot contains the peak at 490 nm and 540 nm for excitation wavelength 340 nm and 440 nm respectively which may be due to the recombination between the sulfur-vacancy-related donor and the valence band [18].



**Figure 8:** PL spectrum of ZnS film for excitation wavelengths of (a) 340 nm and (b) 440 nm

#### 4. Conclusions

Phase pure ZnS thin film was synthesized by CBD using zinc acetate as a precursor material. The technique of CBD is simple, cost effective and offers an easily scalable

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alternative to industrial level. Use of zinc acetate removes the possibility of impurity incorporation in the films. The films are polycrystalline with particle size of  $\sim 15$  nm estimated from line broadening analysis. The result of Tem measurement is in agreement with x-ray analysis. Nearly stoichiometric film could be obtained under optimized concentration. The value of the energy gap of  $\sim 3.85$  eV is near the optimum needs for photovoltaic solar energy conversion. The PL spectra show photoluminescent properties of ZnS thin film.

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