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Zinc Sulfide Thin Film: Structural, Morphological and Optical Study for Photovoltaic Applications

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Abstract: ***Zinc sulfide (ZnS) thin films have been deposited on commercial glass substrates by simple chemical bath deposition technique (CBDT). The Structural, morphological and Optical characteristics of as-deposited films were investigated for the photovoltaic applications. X-ray diffraction study shows the polycrystalline nature of the thin film. The grain sizes obtained by XRD & SEM were well matched. SEM study gives the average grain size between 87nm and 137nm. FTIR and UV-Vis measurement showed that the films had more than 65% transmittance in the wavelength larger than 350 nm, and the fundamental absorption edge shifted to shorter wavelength. Optical study shows the energy band gap ranging from 3.54 to 3.71 eV. The physical conditions were kept identical while growing all the samples. It was found that ZnS films are suitable for various optoelectronic/photovoltaic applications.***
Keywords: ZnS, thin films, zinc sulfide and Optical Properties.

I. INTRODUCTION

ZnS has several advantages in comparison with CdS, such as (i) the band gap of ZnS (3.6 eV) is wider than that of CdS (2.4 eV), which can transmit higher energy photons than the band gap of CdS; (ii) ZnS has a better lattice-matching to CIGS thin film absorbers in the band gap range of 1.3–1.5 eV than CdS. Zinc Sulfide (ZnS) thin film is a promising material for its use in various application devices. In opto-electronics, it can be used as light emitting diode in the blue to ultraviolet spectral region due to its wide band gap of 3.6 eV at room temperature. In the area of optics, ZnS can be used as a reflector and dielectric filter because of its high refractive index (2.35) and its high transmittance in the visible range [1-3].

There are several deposition techniques such as molecular beam epitaxy, plasma chemical sputtering, MOCVD, MOVPE and chemical bath deposition have been used to produce ZnS thin films with adequate properties (high crystallinity, low resistivity and high transmittance). However, Chemical Bath Deposition (CBD) appears as an interesting technique for preparing ZnS thin films, Since CBD is one of the most convenient, reliable, simplest, inexpensive method and useful for large area industrial applications as well as preparation of thin films at close to room temperature. The technique of CBD involves the controlled precipitation from solution of a compound on a suitable substrate. The technique offers many advantages over the more established vapour phase synthetic routes to semiconductor materials, such as CVD, MBE and Spray Pyrolysis. Factors such as control of film thickness and deposition rate by varying the solution pH, temperature and reagent concentration are allied with the ability of CBD to coat large areas, in a reproducible and low cost process. Another advantage of CBD method with respect to other methods is that the films can be deposited on different kinds, shapes and sizes of substrates [4-10].

In the present work we have prepared ZnS thin film using simple CBD technique. As-deposited ZnS thin films having a nanometre grain size. The structural, morphological and optical properties of as deposited thin films have been investigated.

II. EXPERIMENTAL DETAILS

Thin films of ZnS were deposited from a solution of analytical grade with purity over 99.9% of $Zn\ (CH_3COO)_2$ (Zinc Acetate) a Zn^{++} ion source and Thiourea a S^{--} ion source in an alkaline solution of Ammonia. The bath pH was adjusted by the addition of ammonia solution. Commercial glass slides used as substrates were cleaned in acetone and methanol ultrasonically and finally again washed with methanol ultrasonically before use. After cleaning the Substrate were mounted on a glass holder and were immersed in the solution. The solution was continuously stirred at a constant speed during the film deposition with the help of AC motor. The bath temperature was raised to a maximum of 70± 2^oC from room temperature using temperature controller. After the deposition, the ZnS films were washed with methanol ultrasonically to remove the loosely adhered ZnS particles on the film and finally dried in air. The crystallographic structure of films was analyzed with a diffractometer (XPERT-PRO) by using Cu-Kλ lines (λ= 1.54 Å).The average grain size in the deposited films was obtained from a Debye-Scherrer's formula.

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IR spectra of representative sample were recorded with the FTIR-8400S (SHIMADZU, Japan).The absorbance versus wavelength was recorded with the UV-VIS spectrometer (Perkin Elmer: Lambda 35) [11-12].

III.RESULTS AND DISCUSSION

A. Structural properties

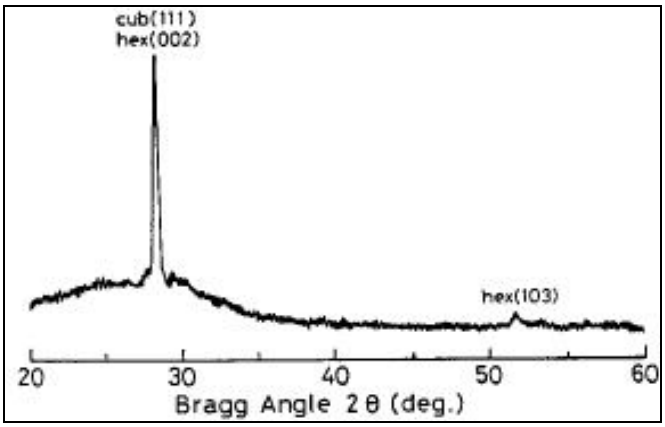

Figure 1 XRD of ZnS thin films

The X-ray diffractogram of ZnS films show broadened diffraction profiles , Fig.1 shows the XRD patterns of ZnS nanoparticles showing reflections from (002), (103) planes , indicating the formation of ZnS nanoparticles having hexagonal structure with cell parameters a=3.800 and c=6.230. The grain size of the nanocrystalline films is estimated using the Scherrer formula,

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

Where, K - a constant taken to be 0·94,

λ - wavelength of X-ray used (λ = 1·54 Å) and

$\beta_{2\theta}$ - full width at half maximum.

The peak broadening in the XRD patterns clearly indicates the formation of ZnS nanocrystal of very small size. The grain sizes were found to be within the range from 08 to 113nm. [12-13],

B. Morphological properties

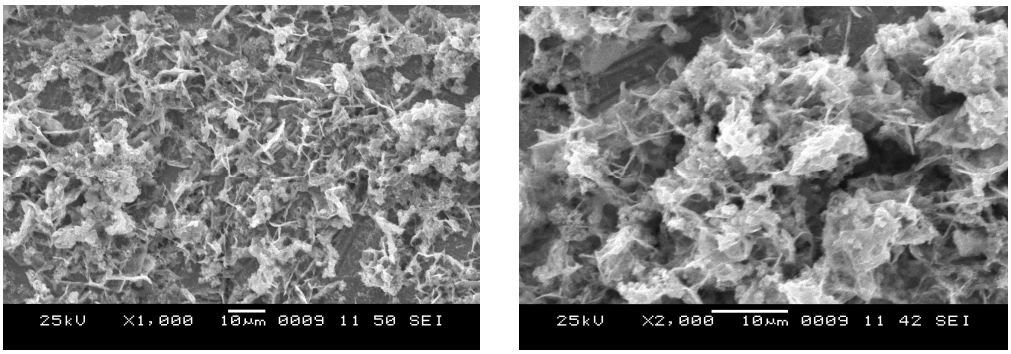

Figure 2. SEM images of ZnS thin film at different magnifications

Scanning electron microscopy (SEM) is a convenient technique to study the nanostructure of thin films. Figure 2 shows the surface morphology of ZnS thin films deposited at 345K temperature observed by SEM. From the micrographs, it is observed that the as-deposited films are not uniform throughout all the regions. But the films are without any void, pinhole or cracks and that they cover the substrates well. From the figure, we clearly observe the small nano sized grains engaged in a fibrous- like structure, which clearly indicates the nanocrystalline nature along with some amorphous phase of ZnS thin films.

C. Infra Red Studies

Fig.3 shows the FTIR spectra of ZnS thin films. The IR frequencies along with the vibrational assignments for ZnS nanoparticles are given in table 1. The band at 3356.25 cm^{-1} are due to O-H stretching vibrations of water molecules. The band at 2746.44 cm^{-1} is due to C-H stretching vibrations (Tang et al 2005).The stretching at 2195.07 cm^{-1} , due to N=N vibrations. At 694·36 cm^{-1} and 705·8 cm^{-1}, there are medium to strong bands which have been assigned to ZnS stretching. [8,10,14].

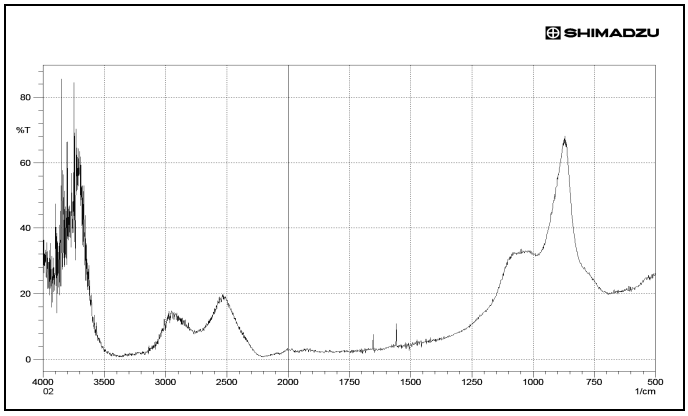

Figure 3. FTIR spectra of ZnS thin film

Table 1 Positions and Vibrational Assignments of ZnS film from FTIR spectra.

Positions (cm^{-1})	Intensities	Assignments
3356.25	Strong	O-H stretching
2754.44	Medium	C-H stretching
2195.07	Strong	N=N stretching
694.40 705.80	Doublet Medium	Zn–S stretching

D. Optical Properties

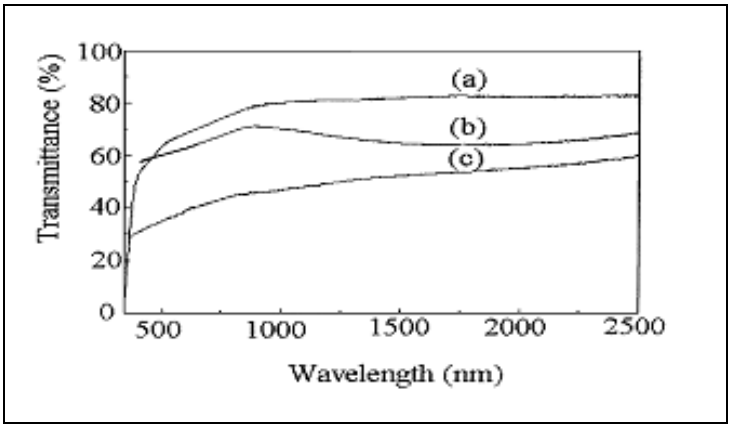

Fig. 4 Optical *Transmittance Vs. wavelength of ZnS thin films*

The optical transmission spectra of as-deposited ZnS thin films taken at room temperature are shown in figure 4. From the spectrograph the absorption edge of the samples are found to occur in the range 250-400 nm for nanocrystalline films. Spectrum clearly indicates shift to the lower wavelength side over bulk crystallites at ~ 500 nm. This blue shift of the absorption edge indicates decrease of the crystallite sizes of the samples. ZnS is a typical direct band gap semiconductor. According to Tauc's relation, the absorption coefficient for direct band material is given by (Tauc 1974; Sharma et al 1992)

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

where, α - the absorption coefficient
c - a constant,
hν- photon energy and
Eg – energy band gap.

A graph between hν vs $(\alpha h\nu)^2$ is plotted and shown in figure 5. The extrapolation of straight line to $(\alpha h\nu)^2 = 0$ axis gives the value of the energy band gap of film materials. The band gap of the films are determined from the plots which are found to be within 3·54eV – 3.71eV. It is observed that the band gap increases with the decrease of crystallite size. The increment in band gap is approximately inversely proportional to the square of the crystallite size based on the effective mass approximation [15-16].

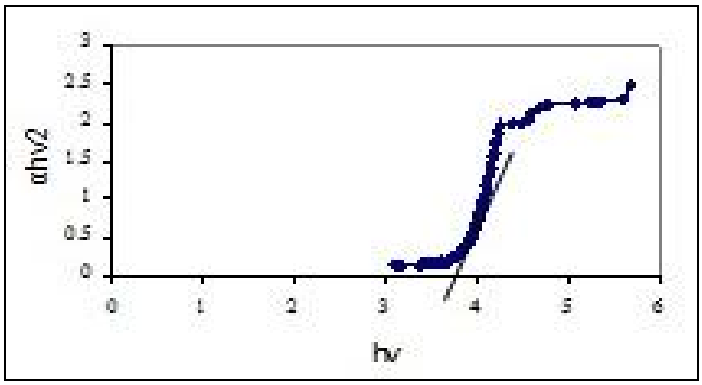

Figure 5. Plot of hν vs $(\alpha h\nu)^2$ for ZnS thin film.

IV. CONCLUSION

Nano-crystalline Zinc sulfide (ZnS) thin films have been successfully prepared by using CBD technique. The crystallite sizes measured by XRD studies are found to be within 87nm to 137 nm. XRD shows that samples are of hexagonal phase which is important for device performance. SEM studies shows presence of long tubes and irregular distributions of particles. FTIR spectroscopy shows the bonding peaks and the percentage transmittance, the films were found to have high transmittance in the range between 60 to 75% in the UV-VISNIR regions; so average 65% transmittance in the wavelength larger than 350 nm are very suitable for use as the buffer layer of thin film solar cells with CuInS2 absorber layer by replacing CdS hence ZnS films are suitable for use as the buffer layer of the CIS solar cells, and it is the viable alternative for replacing CdS in the photovoltaic cell structure. These films could be effective as thermal control window coatings for cold climates and antireflection coatings. The UV absorption studies on films clearly show an increase in band gap with reduction in particle size as compared to bulk materials, and this fact supports the formation of nanocrystallites in these films.

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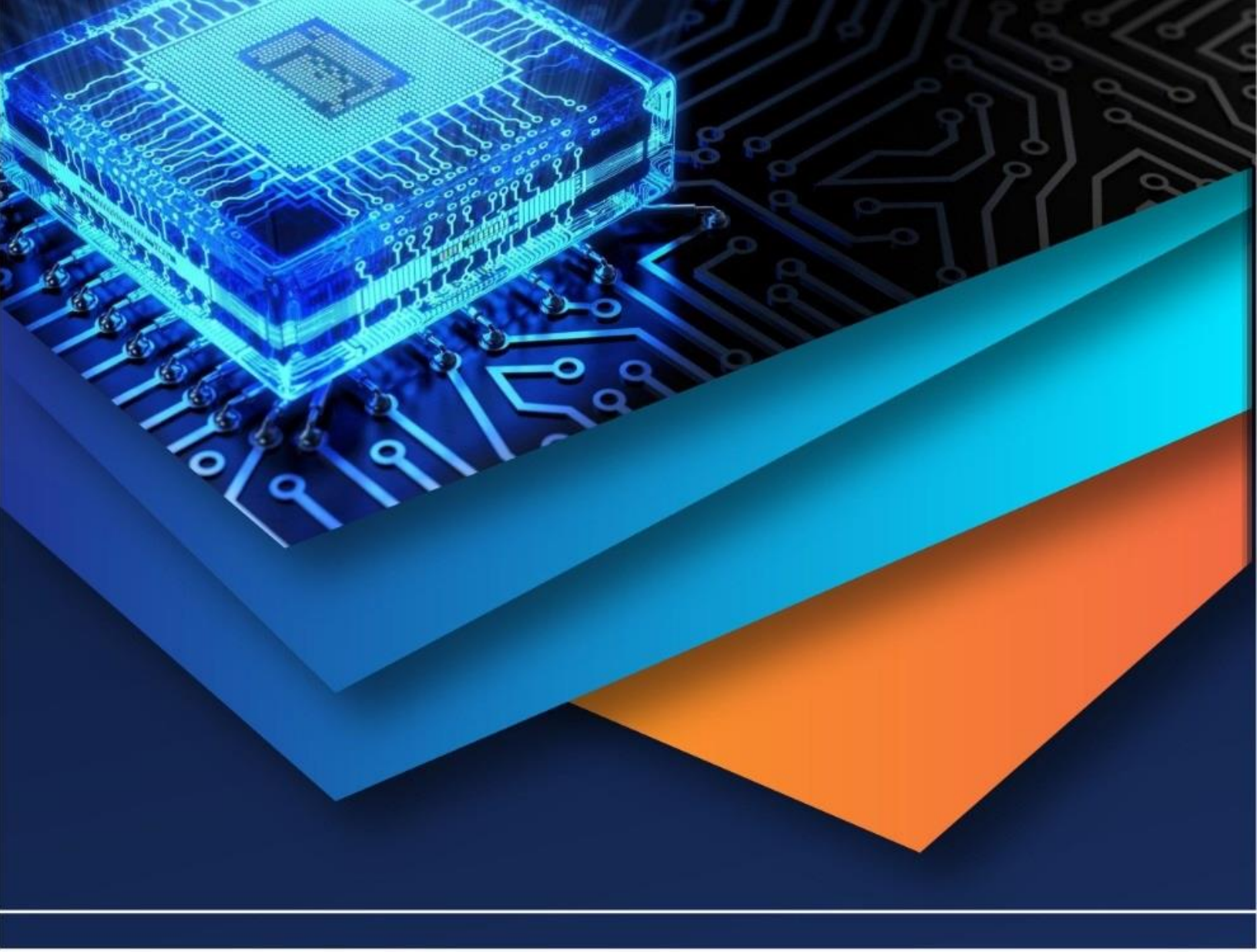

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