Growth, Morphological, Structural, Optical and Compositional Analysis of Zinc Sulphide Thin Film by Dip Coating Method

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Abstract – In this exposure, ZnS thin film has been achieved with purity using zinc nitrate and thiourea as starting precursors. Deposition time behaviour of ZnS on glass plate was studied by morphological study. XRD reveals the sample's crystalline nature and the structural parameters. Optical investigation gave information about the prepared sample. To check the chemical composition of the sample an energy dispersive X-ray (EDS) spectroscopy analysis was preformed.

Index Terms – Zinc Nitrate, Thiourea, Dip Coating, ZnS.

1. INTRODUCTION

Zinc Sulphide (ZnS), a typical II-VI compound semiconductor is showing a bright future in optoelectronic device material because of its wide direct band gap [1]. It has a high refractive index and transmittance in the visible range and is indispensable in the field of photonics. Because of its high refractive index and high transmittance it can be used as a reflector as well as dielectric filter. ZnS thin film has been proven as one of the promising thin film materials for detector, emitter, and modulators in optoelectronics. It is also be used as an antireflection coating for hetero junction solar cells.

In the past, many techniques have been employed to synthesize ZnS nanostructures such as sol-gel [2], dip coating, mechano-chemical [3], reverse micelles method [4], hydrothermal process [5], and chemical co-precipitation reaction method [6]. Among these deposition techniques, dip coating method has been extensively used due to several advantages such as: low cost, low-temperature process and no catalyst assistance. The objective of the present work is to optimize ZnS synthesis conditions for the preparation of ZnS dendrites by using dip coating technique.

2. RELATED WORK

N. Kamoun Allouche, T. Ben Nasr, N. Turki Kamoun, C. Guasch, were prepared Zinc sulphide multilayer films by chemical bath deposition from different host solutions. X-ray diffraction and scanning electron microscopy are used to characterize the structural properties of the films. The surface composition of the films is studied by Auger electrons spectroscopy, and optical properties are studied by spectrophotometric measurements. X-ray diffraction patterns reveal distinct single crystalline phase with preferential orientation along the (1 1 1) plane of the zinc blende structure for the ZnS multilayer. The spacing between (1 1 1) planes of ZnS is well matched to the spacing between (1 1 2) planes of the chalcopyrite $CuInS_2$. After heat treatment all films show a near stoichiometric surface composition as indicated in their AES data. UV–vis measurements show that ZnS multilayer films prepared from the zinc sulphate solution have more than 70% transmission in the wavelengths above 350nm and an optical band gap of about 3.76 eV [1].

Inna Juhnevica et al., synthesized ZnO and ZnO/Al films sol–gel dip coating technique. The influence of annealing regime and dopant concentration on the structural properties of ZnO and aluminium doped ZnO (ZnO/Al) films was investigated. The surface morphology and crystallinity of ZnO films were determined using atomic force microscopy and X-ray diffraction, respectively. The experimental results show that ZnO and ZnO/Al films prepared using "shock" conditions have smooth surfaces and uniform grains. Increase of aluminium concentration led to grain size reduction and denser film [7].

Xiaochun Wu, Fachun Lai, Yongzhong Lin, Zhigao Huang, Rong Chen, were investigated the effects of substrate and annealing temperature on the microstructure, morphology, and optical properties of ZnS films. ZnS films were deposited on glass substrates by an electron beam evaporation system at different substrate temperatures and annealed at different temperatures in air. The structure and morphology of the film were studied by X-ray diffraction and atomic force microscopy. Transmittances of film were measured by spectrophotometer. Refractive indices and extinction coefficients were calculated from all transmittance data. Experimental results show that the as-deposited ZnS film exhibiting cubic structure and the crystallinity is apparently improved with the increase of substrate temperature or annealing temperature. It is also found that film surface changes to ZnO after the film is annealed at 500℃. The average surface grain size and root mean square surface roughness increase with the increase of annealing and substrate temperatures. Additionally, the increase of substrate temperature or annealing temperature will increase the pores in films, which results in the decrease of refractive indices and increase of extinction coefficients of the film [8].

Kumar V et al, prepared ZnS thin films by chemical bath deposition method and studied their optical and structural properties. The ZnS thin films were grown on well cleaned glass substrates by dip and spin coating methods from aqueous solution of Zinc Sulphide and Thiourea at different growth temperatures. The properties of ZnS thin films and their growth mechanisms were studied using x-ray diffraction, UV-Visible spectroscopy and photoluminescence measurements. Effects of deposition techniques on structural and optical properties were reported [9].

3. EXPERIMENTAL DETAILS

The experimental arrangement for the preparing ZnS was shown in figure 1. It consists of a beaker containing 0.4M Zinc Nitrate, 0.7M Thiourea and isoproponol kept at constant temperature (90°C). Distilled water free from impurities was used to prepare the required molar concentrations of chemical 50% of 0.4M Zinc Nitrate and 50% of 0.7M Thiourea. The glass substrate cleaned with 0.1M chromic acid (CrH_2O_4) was used to dip inside the solution.

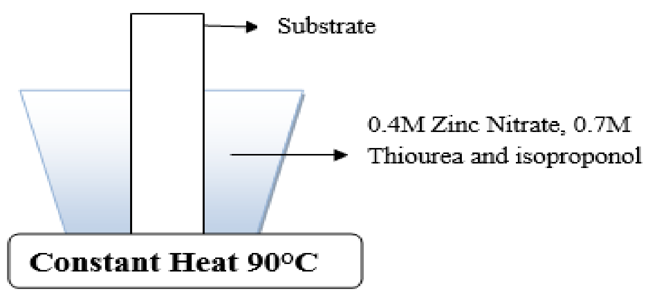


Figure 1: Experimental Arrangement for Preparing ZnS on Glass Substrate.

Figure 2: Prepared ZnS Thin Film

4. RESULTS AND DISCUSSION

4.1 Thickness Measurement

Thickness of the film is found by weight gain method. The mass of the film coated glass plate and the plain glass plate are measured.

The thickness of the film is given by (t) = m/lbd

Where,

m- mass difference=0.01 gm, b- breadth of the film, l- length of the film, d- bulk density of the material.

Thickness = 1.6344 μ m

4.2 AFM Analysis

Microscopic information of prepared ZnS thin films were captured by atomic force microscope for different deposition times (T_d = 50, 100, 150 minutes). In different deposition cases the prepared thin films have good quality, uniform morphology and covered the entire glass substrate's surface.

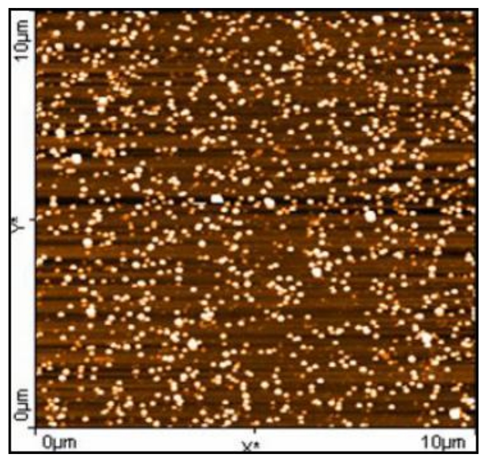


Figure 3: Thin Film of T_d=50 Minutes

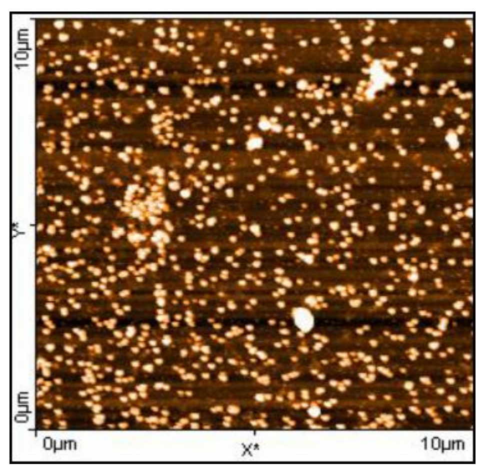


Figure 4: Thin Film of T_d=100 Minutes

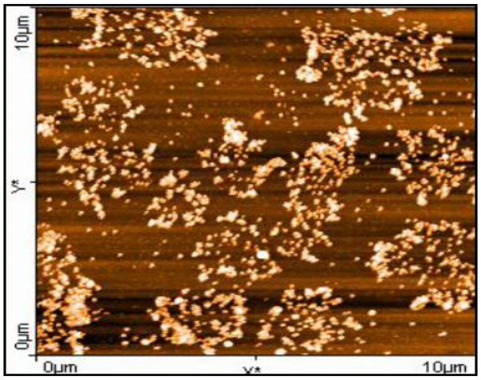


Figure 5: Thin Film of T_d=150 Minutes

When dip coating process was started, the nucleation occurred there and uniformly spherical shaped particles were formed on the surface of the glass plate as shown in figure 3. In the case of T_d = 100 minutes the grain sizes increases and the particles start to aggregate and made clusters. In T_d = 150 minutes case the clusters combined together to make islands. From the results it is well cleared that when the deposition time increases, the thickness of the thin film too increases gradually. Based on T_d the mean grain diameter ranges from 35.4 nm to 197 nm.

4.3 XRD Analysis

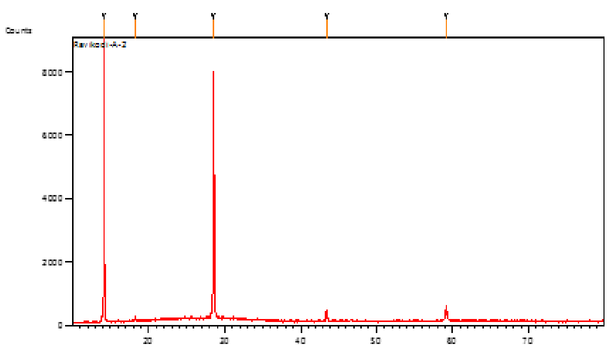


Figure 6: Obtained XRD Result

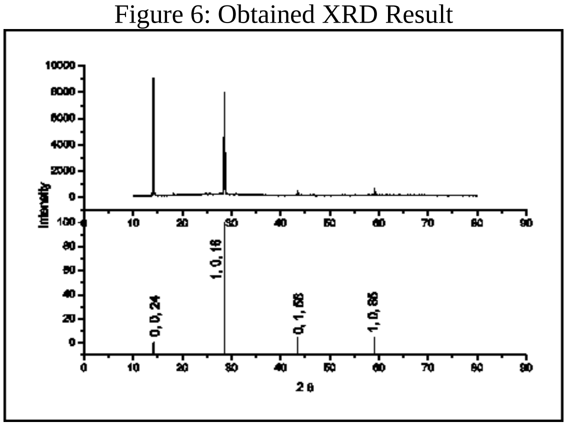


Figure 7: XRD Data Matched with JCPDS Data

The XRD analysis is an inevitable tool in the characterization technique, because it reveals the structure, lattice constant, and other related parameters in the prepared crystalline sample. In the present study XRD spectra was recorded using PAN analytical Diffractometer system (XPERT-PRO) using CU-kα Monochromator. Diffraction data were collected by step scanning oven an angular range 10- 80° (2θ) in steps of 0.01°. The average crystallite size was estimated according to the Scherrer's equations,

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

where λ is the wavelength of CuKα radiation applied (λ = 0.154056 nm), θ is the Bragg's angle of diffraction, β is the full-width at half maximum intensity of the peak observed at 2θ and k is a constant usually chosen ~0.94(shape factor). Recorded XRD pattern of ZnS films shown in figure 6. It is observed that the sample was crystalline in nature, revealing respective peaks at corresponding diffraction angles. Obtained spectra was compared with the standard JCPDS values and found correct for ZnS (JCPDS card no: 89-2426).

Material	Concentration	2θ(degrees)		d-spacing	
		Obs.	Std.	Obs.	Std.
ZnS	0.4 M Zinc Nitrate 0.7M Thiourea	14.185	14.136	6.24	6.260
		28.567	28.585	3.12	3.120
		43.434	43.381	2.08	2.083
		59.135	59.174	1.56	1.565

Table 1: Comparison of Obtained and Standard 2θ, d-Spacing Values

Data	Structure	Lattice Parameter(a)	Lattice Parameter(c)	Volume
My sample	Hexagonal	3.82755	74.9224	950.5698
JCPDS		3.823	74.976	948.99

Table 2: Comparison of Calculated and Standard Lattice Parameters and Volume

The crystallite size of the ZnS nanoparticles was determined by the X-ray line broadening method using the Scherer equation. The calculated particle sizes of the prepared ZnS thin film were 21.813 nm, 17.874 nm, 23.299 nm, 16.583 nm respectively.

Micro strain,

$$\varepsilon = \frac{\beta}{4\tan\theta}$$

$$= 0.13459$$

The micro strain calculation determined the degree of distortion present in the crystallites.

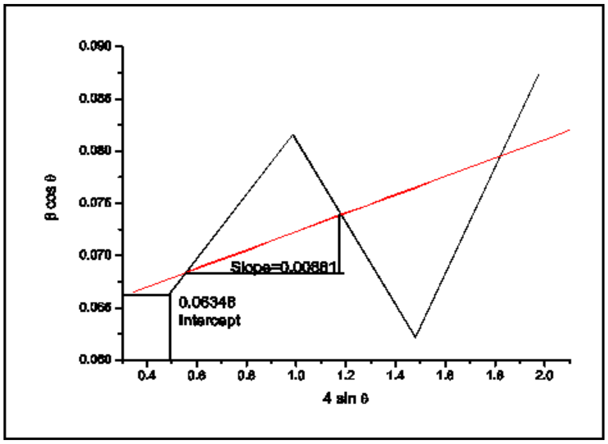
Peak broadening,

$$\beta = \beta\ size + \beta\ strain$$

$$\beta = \frac{0.94\,\lambda}{D\cos\theta} + 4\,\epsilon\tan\theta$$

$$\beta\ cos\theta = \frac{0.94\lambda}{D} + 4\,\epsilon\sin\theta$$

$$= 0.066389 + 0.066386$$



Graph 1: 4 sin θ versus β cos θ (W-H plot)

From graph,

Slope= y/x= 0.00661

D=0.94 λ/Intercept = 22.813

Data	Calculated	W-H Plot
Crystalline size	21.813	22.813
Micro strain	0.13459	0.00661

Table 3: Crystalline Size and Micro Strain from Calculation and W-H Plot

From all the tabulations, it is observed that the 2θ, d-spacing, lattice parameters (a and c), volume are nearly equal to the standard values. The calculated crystalline size and micro strain were also approximately equal to the result from W-H plot.

4.4 Optical Study

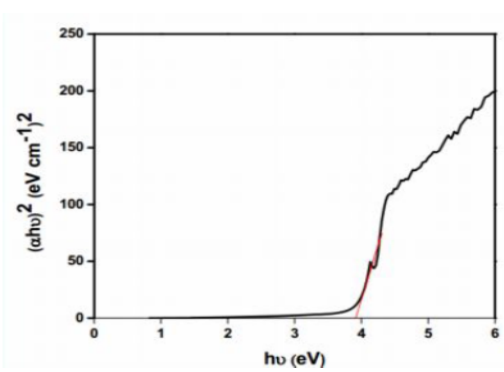


Figure 8: Tauc Plot

The optical band gap E_g can be estimated from the Tauc plot. Figure 8 shows the optical band gap of deposited ZnS. From $(\alpha h\gamma)^2$ versus hγ graph the band gap was founded as 3.92 eV.

4.5 Compositional Analysis

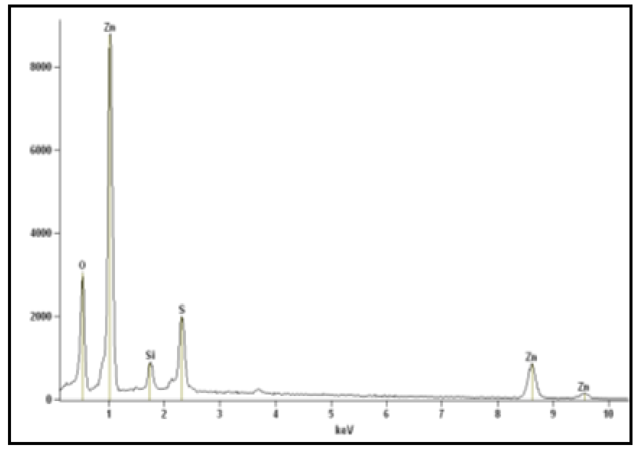


Figure 9: EDS Spectra of Prepared ZnS Thin Film

The compositional analysis by EDS is shown in figure 9. EDS analysis was conducted for ZnS thin film prepared at 150 minutes deposition time. Figure 9 shows that the product contains Zn and S on the glass substrate and no organic residues were merged with it.

5. CONCLUSION

In this paper, we have described the growth, morphological, structural, optical and compositional analysis of prepared ZnS thin film by dip coating technique. Based on different deposition times surface relief was done by the AFM. The structural and phase of prepared ZnS was determined by XRD and compared with the standard values. The optical band gap was obtained from Tauc plot as 3.92 eV. Further the presence of Zn and S was confirmed by EDS.

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