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Effect of substrate temperature on structural, optical and thermal properties of chemically sprayed ZnS thin films

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Zinc Sulfide thin films were successfully deposited on glass substrates by spray pyrolysis method. The films were grown at different substrate temperatures in the range, 300- 400˚C. The effects of substrate temperature on the structural and optical properties were studied. The XRD profiles showed that the films are polycrystalline with cubic structure grown preferentially along the (111) axis. The optical studies exhibit direct allowed transition. Energy band gap vary from 3.43 to 3.80 eV. The thermal behavior of the material has been investigated by TG/DTA and analyses.

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1. Introduction

The deposition of II-VI semiconductors by the spray pyrolysis technique was first investigated by Chamberlin and Skarman [1]. They deposited several of sulfides and selenides in their work on photoconductors. ZnS is a semiconductor with a wide band gap about 3.6 – 3.7 eV, which makes it suitable as a transparent material in the visible region. They exist mainly in two forms, an α-phase (hexagonal wurtzite structure) and a β-phase (cubic sphalerite structure) [2].

Thin films of ZnS find many more applications in the area of optoelectronic device fabrication like UV light emitting diodes [3], blue light emitting diode [4], emissive flat screens [5], electroluminescent devices [6] and antireflection coating in solar cell technology [7]. They are more frequently used for the preparation of ZnS that include metal oxide chemical vapor deposition [8], molecular beam epitaxy [9], chemical bath deposition [10], atomic layer epitaxy [11], RF reactive sputtering [12], pulsed electrochemical deposition [13] and closed-spaced evaporation [14]. Recently more attention has been bestowed on the development of cost effective thin films deposited techniques, especially in the field of photovoltaic technology, for the preparation of device quality alternative absorber and/or buffer layer over large areas in order to economize the technology. In view of this, a simple spray pyrolysis deposition technique is developed for the preparation of ZnS film in the present investigation. This is a low cost and non-wet technique that has good control over the rate of deposition.

In this paper, we present a study of the structural, optical and thermal properties of ZnS thin films prepared by spray pyrolysis technique.

2. Experimental details

Thin films of ZnS are prepared by spray pyrolysis with air as atmosphere. Spray pyrolysis is basically a chemical deposition technique in which fine droplets of the desired material solution was sprayed onto a heated substrate. The experimental setup used for the preparation of pyrolytically spray deposited films is described here. The initial solution was prepared with one part 0.1M Zn $(CH_3COO)_2$ [zinc acetate] and one part 0.1M $SC(NH_2)_2$ [thiourea] in deionized water. Other salts of zinc such as $ZnSO_4$, $ZnCl_2$, $Zn(NO_3)_2$, etc., can be used for deposition. A glass substrate ($2 \times 2 \times 0.1$ cm^3) was used for the preparation of ZnS. The spray time was 30 minutes and pressure was 0.2 kg/cm^3. The substrate temperature varied from 300˚C to 400˚C while other spray parameters were kept constant. The structural study was carried out using Bruker AXS D8 automated X-ray diffractometer with CuKα radiation (λ=1.5405Å). The optical transmittance was recorded using a UV-VIS-NIR Spectrophotometer in the wavelength range 200-1000 nm. Thermal analysis was recorded using SDT Q600 V8.3 Build 101.

3. Results and discussion

3.1. Structural analysis

X-ray diffraction spectra of closely – spaced evaporated ZnS films grown at different substrate temperature T_s, where T_s = 300˚C to 400˚C are shown in the fig. 1. The spectra showed that all the layers grown at different substrate temperatures had only (111) plane appearing at $2\theta \approx 28.48^\circ$ and exhibited cubic structure. In

general ZnS films would crystallize in cubic structure depending on the deposition technique. More recently, Lee et al. [15] and Hichou et al. [16] reported cubic and a combination of cubic and hexagonal phases, for ZnS films grown by chemical vapor deposition and spray pyrolysis techniques respectively.

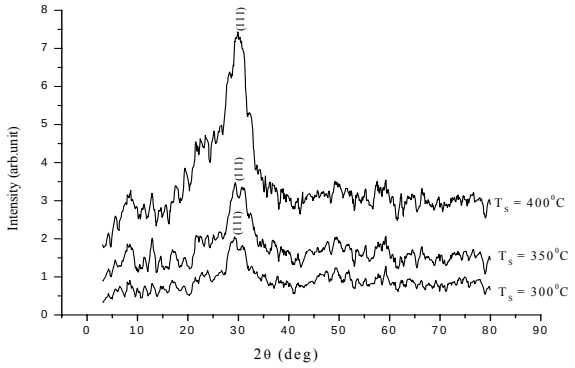

Fig.1 X-ray diffraction pattern of ZnS films at different substrate temperature.

The presence of a single peak at $2\theta \approx 28.80^{\circ}$ indicated that the layers had a highly preferential growth along the (111) direction. However, the films were deposited at higher substrate temperature 400˚C and the diffraction peak was broadened with improved intensity. This was attributed to the re-evaporation of 'sulphur' from the film surface owing to its high vapor pressure. The structural parameters such as interplanar spacing, lattice constant, grain size, strain and dislocation density were determined using appropriate equations given in Table 1. It can be seen from the table that the lattice constant values slightly decreased with deposition temperature and found to be higher than the bulk lattice constant of ZnS, which reveals that the crystallites were under strain [17]. Lattice constant values were calculated for different substrate temperature shown in table 1 and were found to be in good agreement with Joint Committee on Powder Diffraction Standards (JCPDS) values. The variation of grain size, strain and dislocation density for ZnS films with substrate temperature are shown in fig. 2. From the figure it can be seen that the grain size increases with increasing substrate temperature and the strain as well as dislocation density values are found to decrease with increasing deposition temperature.

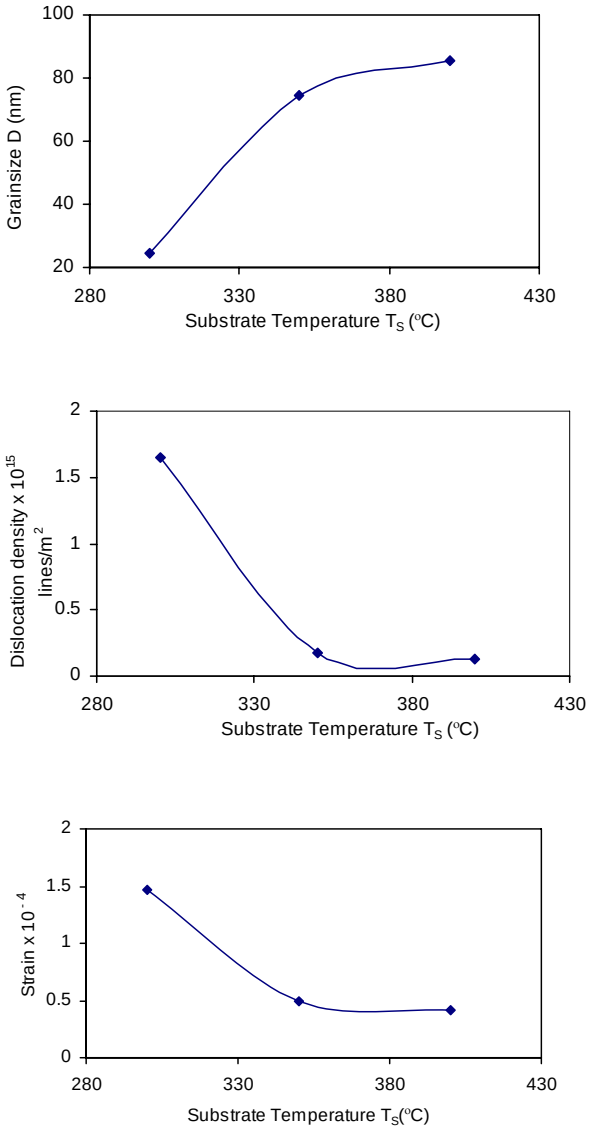

Fig. 2. Variation of structural parameters of ZnS films at different substrate temperature.

Table. 1 Structural parameters of ZnS films formed at different substrate temperature.

Substrate temperature T_S (˚C)	2θ (deg)	d (Å)	h k l	Lattice Constant a (Å)	Grain size D (nm)	Dislocation density× 10^{13} lines/m^2	Strain ε ×10^{-4}
300	28.48	3.1317	1 1 1	5.424	246	1.65	1.47
350	28.75	3.2002	1 1 1	5.420	743	0.18	0.49
400	28.80	3.2174	1 1 1	5.415	855	0.13	0.42

3.2. Optical properties

The optical transmission of the ZnS film is shown in fig.3 for samples prepared at various substrate temperatures for a deposition time 30 min. It can be observed that, in general, an increase in substrate temperature improves the transmission. This improvement can be attributed to the decrease in thickness.

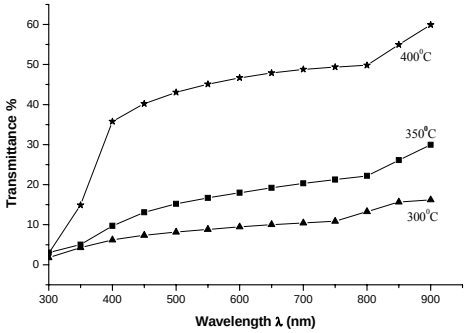

Fig. 3. Transmittance spectra of ZnS films at different substrate temperatures.

The absorption coefficient α and extinction coefficient (absorption index) k_f are obtained from the transmittance T.

$$k_f = \frac{2.303 \times \log (1/T)\, \lambda}{4\pi t}$$

where t is the thickness. The absorption coefficient α is related to the extinction coefficient (absorption index) k_f by

$$\alpha = \frac{4\pi\, k_f}{\epsilon\, \lambda}$$

The optical energy gap of the ZnS thin films was estimated from the optical measurements. The absorption coefficient of pure ZnS is found to follow the relation [18]

$$\alpha = \frac{A\,(h\upsilon - E_g)^2}{h\upsilon}$$

where A is a constant and E_g is the optical band gap. The energy dependence of the absorption coefficient fig.4 indicates that the data fit the above equation and are consistent with a direct allowed inter band transition. By extrapolating to the abscissa, optical energy gaps of 3.43, 3.55 and 3.80 eV are estimated for substrate temperatures of 300, 350 and 400˚C respectively. The estimated values of the band gap are larger than that obtained for amorphous ZnS, E_g = 3.4 eV and the average value E_g = 3.59 eV is above that of the cubic phase E_g = 3.5 eV [18]. Thus the values of E_g indicate that the film is polycrystalline with a structure as indicated by X-ray diffraction [19].

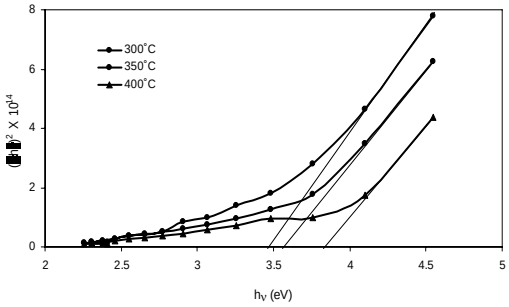

Fig.4 Variation in $(\alpha h\upsilon)^2$ with Photon Energy for ZnS films at different substrate temperatures.

Fig. 5 shows that the absorption coefficient and extinction coefficient decrease with increasing substrate temperature. This may be due to the improvement in the crystallinity with increase in substrate temperature which leads to minimum imperfection [20]. The film thickness decreases with increasing substrate temperature [21]. The estimated optical parameter values are given in table 2.

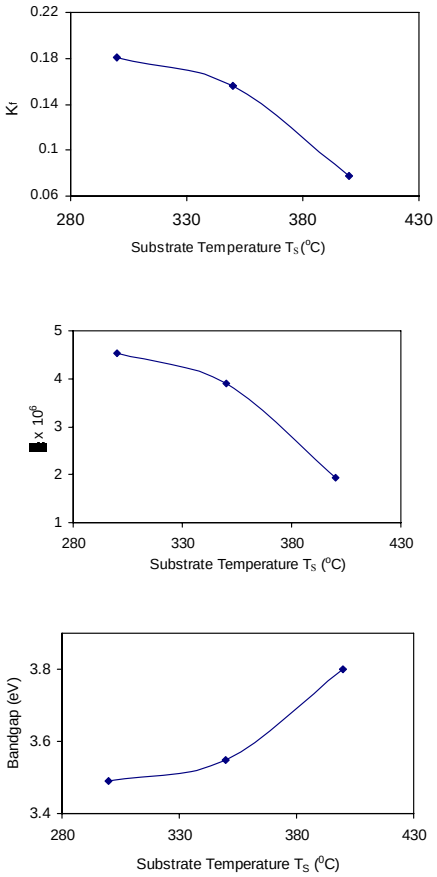

Fig .5 Variation of optical parameters of ZnS films at different substrate temperature.

Table. 2 Optical parameters of ZnS films formed at different substrate temperature.

Substrate Temperature (˚C)	Film Thickness (nm)	Absorption Coefficient (10^6 m^{-1}) (λ = 500 nm)	Extinction Co- efficient (λ = 500 nm)	Band gap Energy (eV)
300	570	4.54	0.18058	3.43
350	540	3.91	0.15558	3.55
400	490	1.94	0.07715	3.81

3.3. Thermal analysis

3.3.1. TG-DTA analysis

The simultaneous TG-DTA thermograms are shown in figs. 6(a) and 6(b) for different substrate temperature 300˚ and 400˚C. The deposited thin films were subjected to the above analysis in nitrogen atmosphere.

The TG thermogram shows the weight loss of 7% due to the moisture loss. Correspondingly the chemical reaction is endothermic in nature as shown by DTA spectrum. On further heating the compounds are decomposition above 481˚C. Decomposition begins at 691˚C at which exothermic reaction is exhibited by DTA spectrum. Correspondingly weight loss was found to be 23%. Again on heating the compound once again started decomposing above 691˚C and the weight loss is 32% as shown in table 3(a) and the reaction mechanism is exothermic.

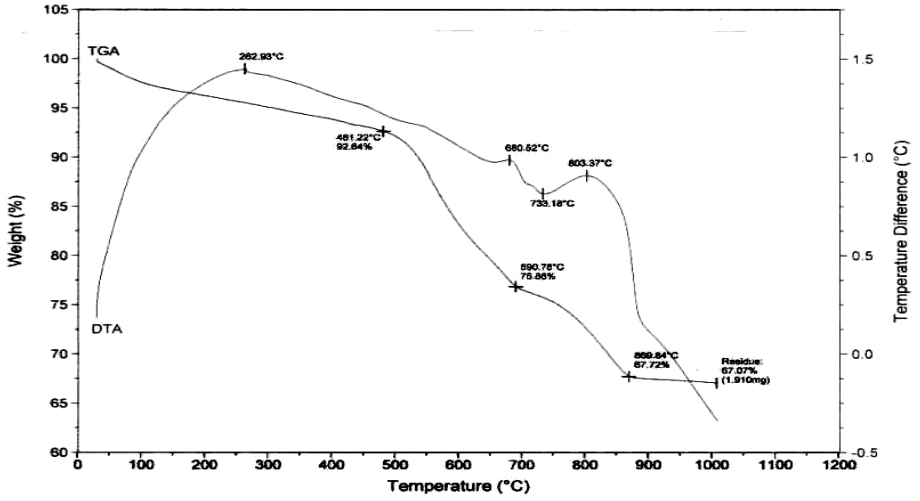

Fig. 6(a) TG – DTA Spectrum of ZnS thin films at substrate temperature 300˚

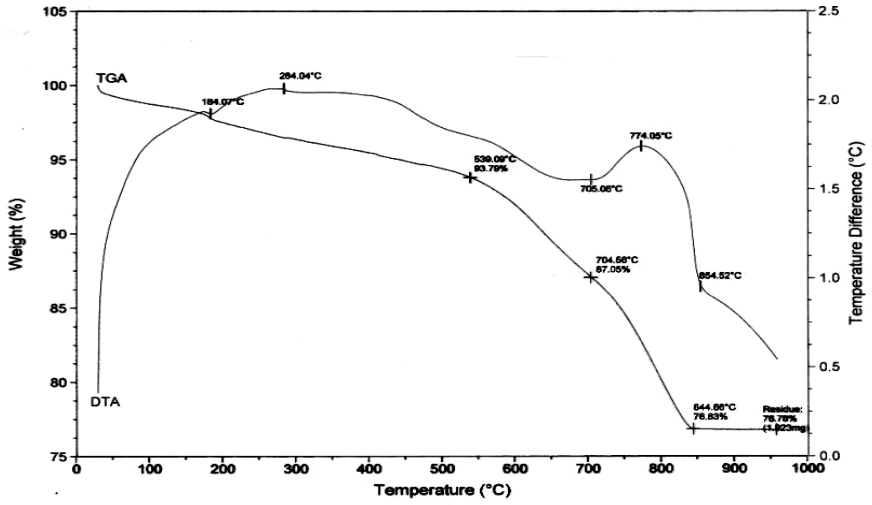

Fig. 6(b) TG – DTA Spectrum of ZnS thin films at substrate temperature 400˚

Table 3(a) TG-DTA analysis for ZnS thin films at substrate temperature 300˚C.

Compound	DTA Peak Temperature (˚C)	Thermogravimetry (TG)		Decomposition Phenomenal Product
		Temperature Range (˚C)	Mass Loss (%)	
Zinc Sulphide	263 (+)	25-481	7%	Moisture loss
	680 (-)	481-691	23%	Zinc nitrite(Zn_3N_2)
	803 (-)	691-870	32 %	Sublimation

While the substrate temperature at 400˚C no change in weight loss were observed upto 705˚C. but on further heating the slight increase in weight loss 38% was observed and at temperature range 844˚C the reaction mechanism is endothermic as shown in table 3(b).

Table 3(b) TG-DTA analysis for ZnS thin films at substrate temperature 400˚C

Compound	DTA Peak Temperature (˚C)	Thermogravimetry (TG)		Decomposition Phenomenal Product
		Temperature Range (˚C)	Mass Loss (%)	
Zinc Sulphide	552 (+)	25-539	7%	Moisture loss
	774 (-)	539-705	23%	Zinc nitrite(Zn_3N_2)
	854 (+)	705-844	38 %	Sublimation

3.3.2. DSC analysis

The DSC measurements were made in the temperature range 0˚ to 1000˚C with heating range 20˚C/min in N_2. In the present work SDT Q600 V8.3 Build 101 was used. This differential scanning calorimeter has a temperature accuracy of ± 0.2˚C temperature reproducibility ± 0.1˚C and sampling rate maximum 10values/sec. since the DSC was interfaced with computer the recorded spectrum is obtained from the computer. The DSC curve for deposited thin films for a different substrate temperature 300˚ and 400˚C as shown in figs.7(a) and 7(b). The peak corresponding to 682.52˚C is positive which confirms the reaction is exothermic in nature as shown in fig.7 (a) corresponding to 300˚C. For 400˚C the reaction mechanism is found to be the same as that of in the DTA analysis.

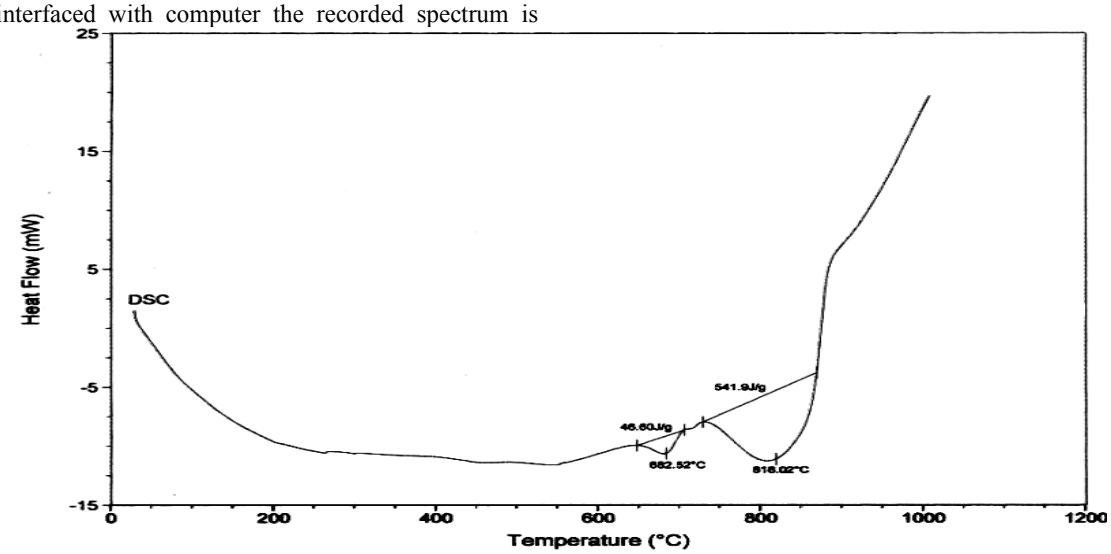

Fig.7(a) DSC Spectrum of ZnS thin films at substrate temperature 300˚C

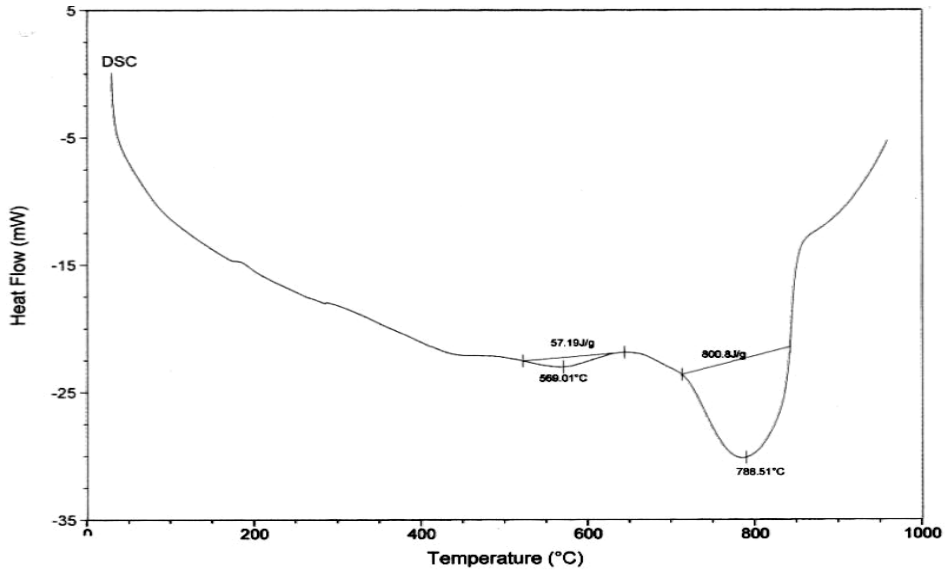

Fig.7 (b) DSC Spectrum of ZnS thin films at substrate temperature 400˚C

4. Conclusions

ZnS thin films were successfully deposited using spray pyrolysis method at different substrate temperatures that varied from 300 to 400˚C. Highly crystalline and cubic ZnS films with only (111) plane was deposited at 400˚C. Optical studies show that the transmittance and band gap energy increases with increase in substrate temperature. The variation of band gap energies from 3.43 to 3.80 eV is high enough for the utilization of these films in solar cell applications. The thermogram analysis showed the decomposition range of the deposited ZnS thin films material and correspondingly the DTA spectrum exhibited the appropriate chemical reaction mechanism. Chemical reaction mechanism revealed by DTA analysis is in good agreement with the DSC analysis.

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