Effect of temperature on ZnS thin film by Chemical Spray Pyrolysis Technique

A. D. Kanwate & E.U. Masumdar
Department of Physics, Shri. Vyankatesh College, D.Raja-443204, Maharashtra, India
Department of Physics, Rajarshi Shahu College, Latur - 413512, Maharashtra, India

Abstract:

In this paper, study the effect of substrate temperature on thickness, Structural, Morphological and Electrical properties of ZnS thin film were studied. From the X-ray diffraction pattern at substrate temperatures in the ranges from 425^{0}C-500^{0}C with difference of 25^{0}C which shows a good crystallinity is obtained with cubic crystal structure. From surface morphology of ZnS thin film prepared at a substrate temperature 500^{0}C is relatively more homogeneous, good stoichiometry, a smooth surface. It was found from electrical properties the electrical resistivity (ρ) of the given ZnS film at substrate temperatures 425^{0}C is 5.58 × 10^6 Ω-cm, 450^{0}C is 4.4×10^6 Ω-cm, 475^{0}C is 4.06×10^6Ω-cm, and 500^{0}C is 2.4×10^6 Ω-cm.

Keywords: Spray pyrolysis, thickness, structural properties, Morphological properties & electrical properties.

1. Introduction:

ZnS can be used as an antireflection coating (n-window layers) in hetero-junction in solar cells as the wide bandgap decreases the absorption losses and increases the short circuit current of the cell. ZnS thin film material used for various application devices in solar cell. It was also used in LED for blue to ultra violet spectral region due to its wide band gap 3.6-3.7ev at room temperature. ZnS thin films are extensively used in industry for various purposes such as filter, reflected film, dielectric film and photoelectric cell with adequate properties [1].

ZnS thin films have been prepared by a variety of techniques, such as molecular beam epitaxy [2], chemical bath deposition [3], thermal evaporation [4] and RF reactive sputtering [5] etc. The technique of spray pyrolysis also offers interesting possibilities for preparing ZnS thin films. Indeed, this technique for the preparation of thin films is very attractive because it is inexpensive, simple and capable of depositing optically smooth, uniform and homogeneous layers. Furthermore, because this simple coating technique involves processing in an ambient atmosphere, it is easy to incorporate it into an industrial production line [6]. With spray pyrolysis, the solution is sprayed directly onto the substrate. A stream of gas (compressed air) is used for atomization of the solution through the nozzle. The main factors in determining the final physical and chemical properties of the films are the initial solution, the nozzle pressure, and the substrate temperature, among other parameters [7].

H.H. Afifi [1] et.al studied structural properties of ZnS thin film, he was found that a cubic phase structure prepared by spray pyrolysis. Evren Turan [6] studied structural, optical and electrical properties, from that study he found crystallized in a wurtzite structure, a direct band gap energy of 3.62 eV and values of the electrical conductivity and carrier concentration were about $3x10^{-10}$ Ω^{-1} cm^{-1} and $1x10^7$ cm^{-3}, respectively. B. Elidrissi [7] et.al studied structural, compositional and optical properties and he found that films of ZnS with mixture of hexagonal and cubic phases have been prepared by the spray pyrolysis method, found that relatively good film crystallinity was obtained at substrate temperature of 500^{0}C deposition time of 35 min and spray rate of 5ml min^{-1} and these films are also nearly stoichiometric with a slight deficiency in sulphur. Furthermore, these films have a transmittance of about 75% in the visible and near

infrared region. M.C. Lopez [8] et.al were studied surface morphology, he was found a good stoichiometry, a smooth surface, a transmission higher than 80% in the visible region and a characteristic diffraction signal at $2\theta = 28{:}95^0$. Thin films of ZnS with mixture of hexagonal and cubic phases, transmittance of about 75% in the visible and near infrared region have been prepared by the spray pyrolysis method.

In the present study we report the effect of temperature on the thickness, structural, morphological and electrical properties ZnS thin films for application as an antireflective coating in solar cells.

2. Experimental Work:

Chemical spray pyrolysis techniques is very interesting method of depositing ZnS thin films due to the fact that it simple, convenient, cost effective, capable of producing uniform and homogeneous films that can produced to industrial scale. ZnS thin films prepared on glass substrate (7.5cm×2.5cm) using homemade spray pyrolysis technique with different temperatures ranges of 425-500^{0}C with a difference of 25^{0}C. Before deposition the glass substrate were boiled in chromic acid for 15 min. & washed with lebalene. Then after substrate were ultrasonically cleaned for 10 min.

The precursor solutions were used for the deposition of ZnS thin films 0.25M equimolar solution of Zinc Chloride ($ZnCl_2$) and Thiourea ($CS(NH_2)_2$) in double distilled water. The solution are mixed together and used for deposition with spray rate 4ml/sec. onto a glass substrate. Compressed air pressure is used as carrier gas to spraying a solution. The spray deposition films are, in general strong and adherent, mechanically hard, pin hole free and stable with time and temperature.

3. Result and discussion:

3.1 Thickness Measurement:

Thickness of deposited film can be calculated by Gravimetric method. Thickness of film is can be measure by formula

$$t = \frac{\Delta m}{l * b * \rho} \quad \ldots\ldots\ldots\ldots (1)$$

Where Δm= Weight difference, l= length of substrate, b= breadth of substrate, ρ= density.

Thickness of the samples was measured using Gravimetric method. The observed thickness of thin film at temperatures for 400^{0}C is 1.397 µm, 425^0 C is 1.016 µm, 450^{0}C is 1.000 µm, 475^{0}C is 1.120 µm and for 500^{0}C is 0.624 µm. In the present work, it is concluded if we increase substrate temperature from 400-450^{0}C, then thickness of deposited film will decreases.

3.2 X-Ray Diffraction Analysis (XRD):

X-Ray diffraction pattern of ZnS thin films prepared at various temperature (T_s = 425-500^{0}C) with CuKα radiation (1.54060A^0). The XRD pattern (JCPDS card no.75-1560) obtained for the ZnS films grown on glass substrates were studied in 2θ ranges 10^0-90^0. Fig.2 shows the XRD pattern of the ZnS thin film deposited on to a glass substrate at various substrate temperature ranging from 425^{0}C to 500^{0}C.

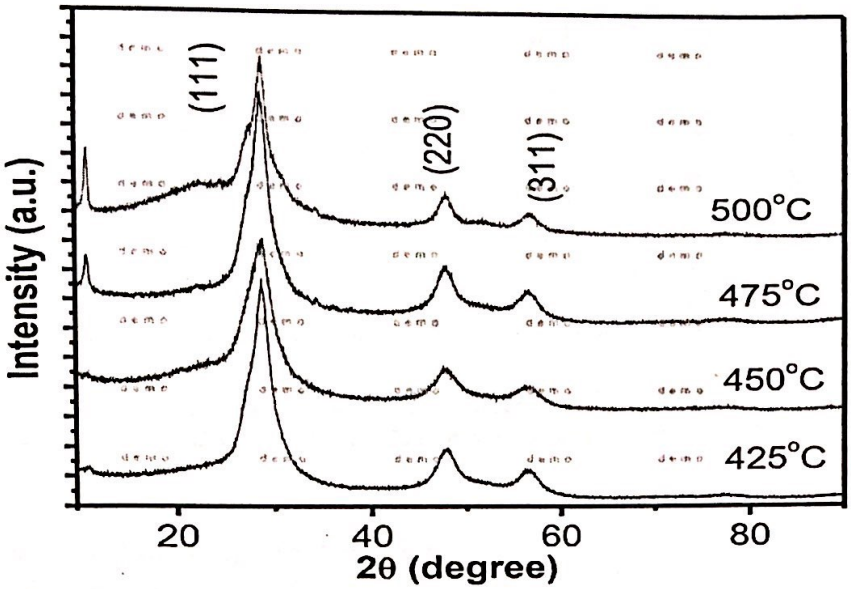

Fig. 1 XRD pattern of ZnS thin film deposited at various substrate temperatures.

From X-ray pattern found that at temperature 500^{0}C, a well crystallized films was obtained. The three peaks corresponds to the (111), (220) and (311) lattice planes with 2θ values respectively. As the substrate temperature increases the intensity of ZnS (111) peak increase and becomes narrower indicating an improvement of crystallinity. The overall intensity of the reflections increased when the substrate temperature for deposition increased without the appearance of any new reflections. Thus, no other phases were formed by raising the substrate temperature but only the crystallinity of the formed phase was improved. As given JCPDS data revealed that only cubic crystal structure ZnS was formed. Further d-values where calculated by calculating θ values from the peaks of the X-ray spectrum using Bragg's relation;

$$2d\sin\theta = n\lambda \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where, n = 1 (first order), λ = wavelength of X-ray (1.54060 A^0)

The value of average crystallite size of as deposited ZnS thin film estimated by using Scherrer's formula given as,

$$D = \frac{k\lambda}{\beta\cos\theta} \quad \ldots\ldots\ldots\ldots (3)$$

Where, k is constant, λ is the wavelength of X-ray, β is full width at half maximum in radian and θ is Braggs angle.

Substrate Temp.(^{0}C)	2θ Degree	d (A^0) calculated	d (A^0) standard	Planes	Crystalline size D (nm)
425	28.70	3.108	3.086	111	3.80
	48.11	1.890	1.890	220	
	56.70	1.622	1.612	311	
450	28.80	3.097	3.086	111	4.43
	47.54	1.911	1.890	220	

	56.14	1.637	1.612	311	
475	28.68	3.110	3.086	111	4.25
	47.58	1.909	1.890	220	
	56.26	1.634	1.612	311	
500	28.08	3.175	3.086	111	5.11
	47.88	1.898	1.890	220	
	56.52	1.627	1.612	311	

Table.1: X-ray diffraction data of spray deposited ZnS thin films at various substrate temperatures.

From the above table.1 it was found that crystalline size (D) increases from 3.8nm to 5.11nm with increase in temperature from 425^{0}C to 500^{0}C. That means as temperature increases crystallinity of the film increases.

3.3 Scanning Electron Microscope Analysis (SEM):

The surface morphology of ZnS thin film was studied by Scanning Electron Microscope (at accelerating voltage of 20kV). Fig. 3 (a), (b), (c) and (d) shows the surface morphology of ZnS thin films deposited at various substrate temperatures ranging from 425-500^{0}C.

As we seen in figure the surface morphology of ZnS thin film prepared at a substrate temperature 500^{0}C is relatively more homogeneous and dense with no cracks. On the other hand, the film deposited at substrate temperatures 425^{0}C, 450^{0}C and 475^{0}C has inhomogeneous surface with some cracks like structure.

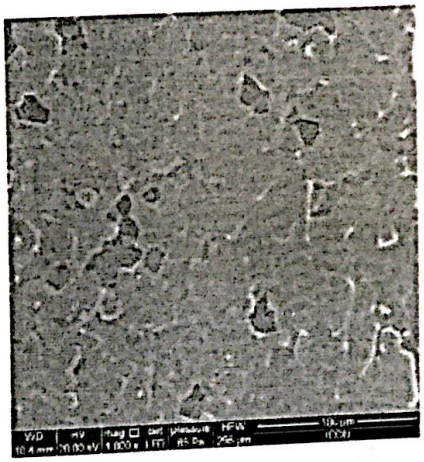

Fig. (a) X 1000 magnification

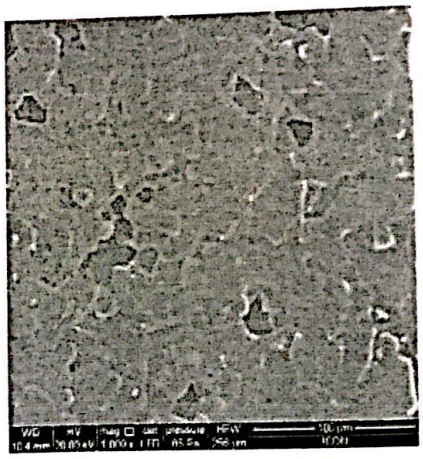

Fig. (b) X 1000 magnification

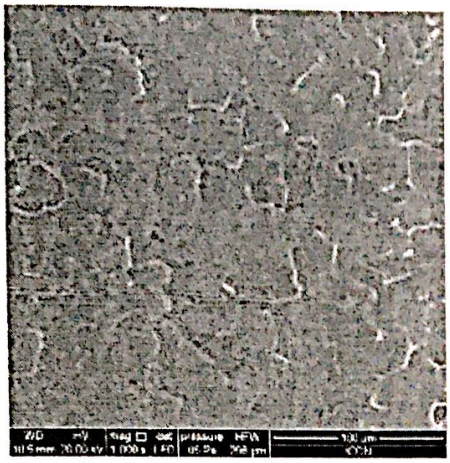

Fig. (c) X 1000 magnification

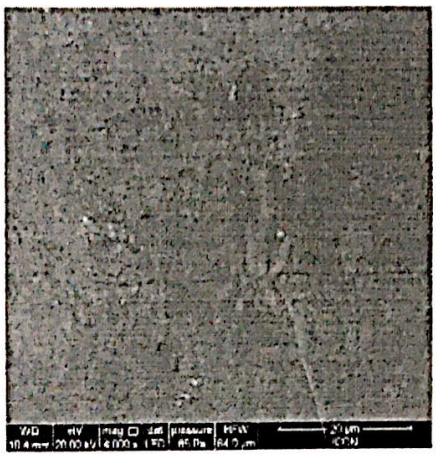

Fig. (d) X 1000 magnification

Fig. 2: SEM images of ZnS (a), (b), (c), and (d) at temperature 425^{0}C, 450^{0}C, 475^{0}C and 500^{0}C with various magnification.

From surface morphology of ZnS thin film prepared at a substrate temperature 500^{0}C is relatively more homogeneous, good stoichiometry, a smooth surface.

3.4 Electrical Resistivity:

The DC electrical resistivity of the ZnS films was measured as a function of temperature in the range 425^{0}C-500^{0}C using two point probe method. The variation of log ρ versus inverse of absolute temperature (1000/T) for deposited ZnS thin films are shown in Fig.4 electrical resistivity (ρ) of the given ZnS film at substrate temperatures, 425^{0}C-500^{0}C is 5.58 × 10^6 Ω.cm, 4.4 ×10^6 Ω-cm, 4.06 × 10^6 Ω-cm and 2.4 × 10^6 Ωcm respectively. It is observed that the resistivity of ZnS films was decreased with increase in temperature, indicating a semiconducting electrical behavior. It is shows that all the films are semiconducting. It is found that resistivity decreases continuously with increasing substrate temperatures.

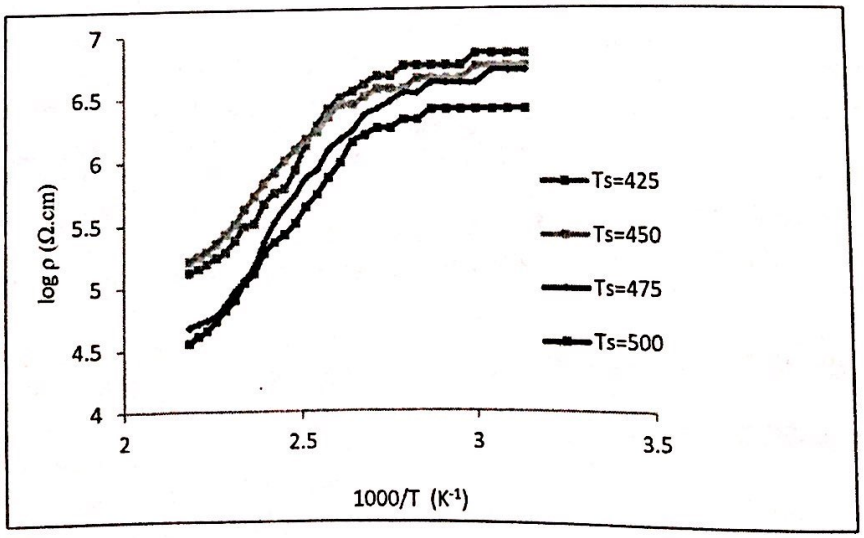

Fig.3: Variations of log ρ vs inverse of absolute temperature (1000/T) for ZnS thin films.

4. Conclusion:

ZnS thin films were prepared by home-made chemical spray pyrolysis with varying temperatures from 425^{0}C -500^{0}C. The precursor solutions were used for the deposition of ZnS thin films as Zinc Chloride ($ZnCl_2$) and Thiourea (CS $(NH_2)_2$) in double distilled water. We studied the thickness, structural, morphological and electrical properties of ZnS thin film. The observed thickness of thin film at temperatures for 400^{0}C is 1.397 µm, 425^0 C is 1.016 µm, 450^{0}C is 1.000 µm, 475^{0}C is 1.120 µm and for 500^{0}C is 0.624 µm. From Structural studies ZnS film form a cubic crystal structure, as temperature increase the crystalline size (D) of the film increases from 3.8nm to 5.11nm. From surface morphology of ZnS thin film prepared at a substrate temperature 500^{0}C is relatively more homogeneous, good stoichiometry, a smooth surface than other temperature. The electrical resistivity (ρ) of the given ZnS film at substrate temperatures, 425^{0}C-500^{0}C were found to be 5.58 × 10^6 Ω.cm, 4.4 ×10^6 Ω-cm, 4.06 × 10^6 Ω-cm and 2.4 × 10^6 Ω-cm respectively. This makes ZnS thin films prepared by spray pyrolysis more appropriate materials for various applications.

Acknowledgement

One of the authors A.D. Kanwate is grateful to the CSIR, New Delhi, India for the financial assistance through the Junior Research Fellowship (File No. 08/595(0002)/2015-EMR-I).

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