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Influence of Annealing Temperature on the Characteristics of Chemical Bath Deposited Zinc Sulphide Thin Films for Solar Cell Applications

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Abstract: *Zinc Sulphide(ZnS)thin films which are transparent and well adhered on glass substrate were obtained by Chemical Bath Deposition method. The annealing temperature was varied from 200 °C to 300°C and the influence of annealing temperature on the structural characteristics of nano structured Zinc sulphide thin films were reported. The parameters such as pH, bath temperature were kept constant and the other parameters such as dipping time, concentration of the solution and annealing temperature were varied. The SEM images show that for a particular combination of parameters, ZnS nano flowers were formed and the same has been kept as optimum condition for coating ZnS thin films. Absorbance and transmittance of ZnS thin films were measured using UV-Vis Spectrometer. Nano ZnS thin films show high transmittance in the visible region and was found to have band gap to be in the range of 3.5- 3.98 eV. ZnS thin films coated for 90 mins with a solution concentration of 0.025 M were found to have large band gap and the same has been fixed as optimum combination of parameters for coating ZnS thin films. ZnS thin films annealed at 200 °C had good adherence to the glass substrate and also high value of transmittance and band gap. These n-type ZnS thin films can be used for the preparation semiconductor devices for solar cell applications.*

Keywords: Zinc Sulphide thin films; Solution Concentration; Annealing Temperature; Transmittance.

1. INTRODUCTION

Research on solar cell fabrication aims at fabrication of low cost devices in order to reduce the cost of energy obtained. These resulted in focusing attention on thin films technology and nanoparticles coating for solar cell fabrication [1]. Zinc Sulphide (ZnS) is an n-type II-VI compound having a wide band gap value of (3.5 – 3.9eV) at room temperature [2] . ZnS has found to have potential applications in blue light emitting diodes, electroluminescent devices and photovoltaic cells [3-5] . Researchers all over the world are focusing on 2D nanostructure P-N junctions for their potential applications in Photovoltaic devices. There are a number of techniques available for the preparation of metal sulphide thin films such as Sputtering [6] , Chemical Vapour Deposition [7], Spray Pyrolysis [8] , Electro deposition [9], Successive Ionic adsorption and reaction [10] and Chemical Bath Deposition [11-14].The deposition of ZnS thin films by Chemical Bath Deposition (CBD) is cheaper and simpler method and the same is reported in this paper. The quality and purity of large area ZnS films obtained by this method is high compared to other method[15]. The repeatability and low cost of coating metal films using CBD has been its centre of attraction [16]. Numerical study of the solar drying of sewage sludge with the climatic conditions of a particular region and showed the variation of drying rate for different days [17]. Three methods which can be used to convert low (80 to 150 °C) or intermediate(up to 350 °C) temperature thermal energy into mechanical work and electricity [18].The effect of independent parameters such as Reynolds number ranging from 10 to 150 and nanoparticles volume fraction ranging from 0 to 0.04 were studied on the flow field and heat transfer in micro channels [19-20] . The use of aqueous alkaline baths for the deposition of ZnS thin films has been reported by many researches[21-24].

These papers report bulk and thin film characteristics of ZnS which include its electrical and optical properties. Optical constants such as refractive index and extinction coefficient are the most important parameters which determine the optical properties of the films prepared. It can be determined by measuring absorbance and transmission using UV-vis spectrometer. The amount of light transmitted through the thin film materials depend on the amount of reflection and absorption that takes place along the path of light [24-25]. Godwin investigated about the optimum parameters for obtaining the best performance using alternate fuels of IC engines working under the current cooling system using Nanofluids [26].

2.EXPERIMENTAL

Glass substrates (75mmx 25mmx1.35mm) were first degreased with ethanol for 10 min followed by Ultrasonic cleaning with dou-

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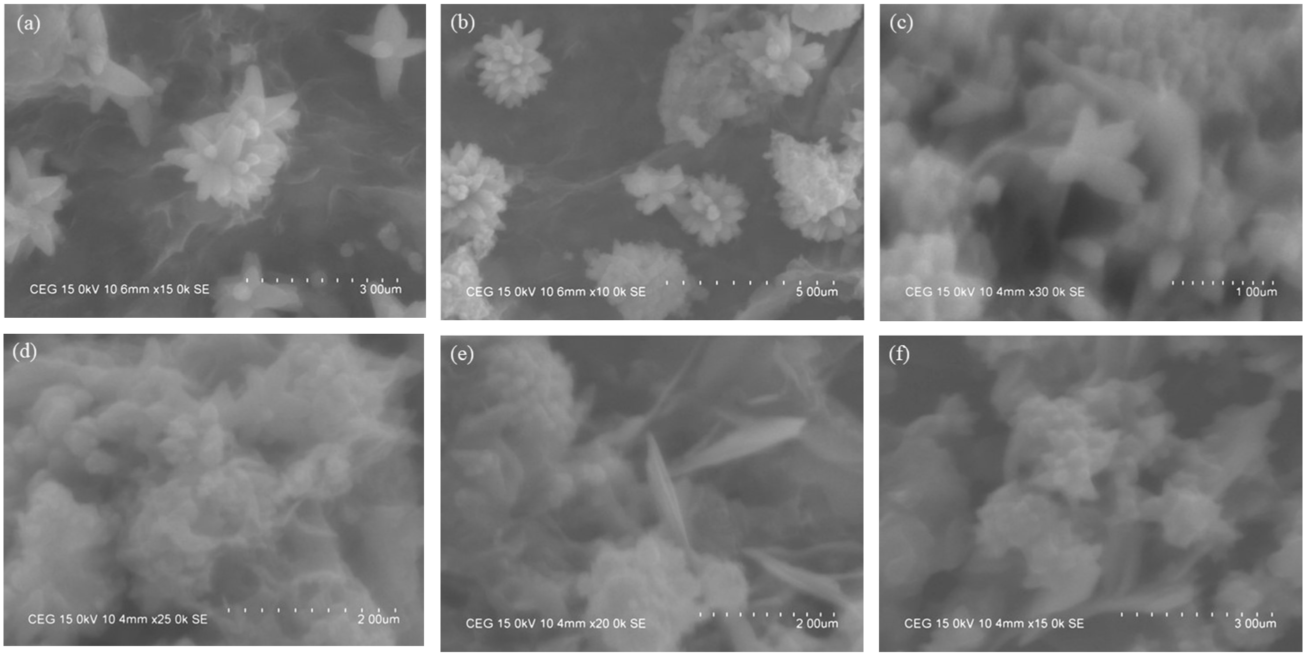

Figure 1. SEM micrographs of samples (a) L_2 (b) L_3 (c) L_5 (d) L_6 (e) L_8 (f) L_9

ble distilled water for 10 min. After that the substrates were immersed in Chromic acid for 24 hours. Finally, the substrates were washed and rinsed with de-ionized water and then dried.The Chemical Bath Deposition (CBD) of ZnS in aqueous bath begins with the complexation of Zinc cations by using complexing agent such as ammonia and the consecutive reaction with the sulphide ions obtained by the hydrolysis of Thiourea. Film deposition was carried out by mixing 20ml of 0.27M Thiourea (SC $(NH_2)_2$ solution, 20 ml of 0.025 M Zinc Sulphate ($ZnSO_4$) solution and 25% ammonia (NH_4OH) solution. The concentration of ($ZnSO_4$) solution was varied from 0.025 M to 0.035 M and the sample details were given in L9 array table [26-30] (Table1).To optimize the parameters to get better ZnS films, we varied solution concentration, dipping time and annealing temperature and parameters such as bath temperature and pH were kept constant at 90°C and 10 respectively. Glass substrates were immersed in the beaker containing the precursor solutions with different combinations and thin films were deposited by varying dipping time (30, 60, 90 min) and were annealed. The annealing of the final samples was done at different temperatures 200°C, 250 °C and 300 °C.The annealed samples were characterized for their structural ordering using X-ray Diffractometer which utilizes Cu-Kα radiation of wavelength 0.15418 nm.Band gap of ZnS thin films were measured using UV-vis spectrometer. The surface morphology was investigated by obtaining the images from Scanning Electron Microscope.

Table. 1

Sample	$ZnSO_4$ Concentration	Dipping time (min)	Annealing temperature (°C)
L_1	0.025	30	300
L_2	0.025	60	250
L_3	0.025	90	200
L_4	0.030	30	250
L_5	0.030	60	200
L_6	0.030	90	300
L_7	0.035	30	200
L_8	0.035	60	300
L_9	0.035	90	250

3. RESULTS AND DISCUSSION

3.1. Morphological studies

The micro- structural surface topography were investigated using Scanning Electron Microscope (SEM). Figure 1(a) and 1(b) shows SEM micrographs of samples L2 and L3. These micrographs reveal that more nano flowers of size 100 nm were formed in sample L3 than in sample L2 which shows the influence of dipping time. Longer the dipping time, greater is the formation of Nano flowers. We investigated the role of solution concentration on the formation of Nano flowers with constant dipping time. SEM images of samples L_5 and L_6 are shown in Figure 1(c) and 1(d) clearly reveals that no Nano flowers were formed. With further increase in the concentration with same dipping time, it was found in samples L_8 and L_9. nano flowers were formed along with nano rods Dispersed nano flowers were observed in samples coated with 0.025M concentration whose size are around 100nm, for films prepared by 0.025 M compared to 0.035 M of Zinc sulphate.The composition of the thin films formed by CBD was confirmed by using EDX analysis. Figure 2 shows EDX spectra of sample L_3 which showed evenly dispersed nano flowers.EDX spectra of sample L_3confirms the composition of the is found to be Zinc, Sulphur and Oxygen which is expected from that of ZnS thin films. Zinc is the main composition in the deposited thin films followed by sulphur. Figure 3.shows the EDX analysis of sample L_9. It can be seen from Fig. 2 and Fig. 3 that the percentage of Zinc in sample L_3 is more than that in the sample L_9.

3.2. Structural analysis

Structural ordering of thin films are investigated through XRD measurements in the range of angle 2θ between 20° to 80° as shown in figure 4. For all the ZnS thin film samples, main peak is

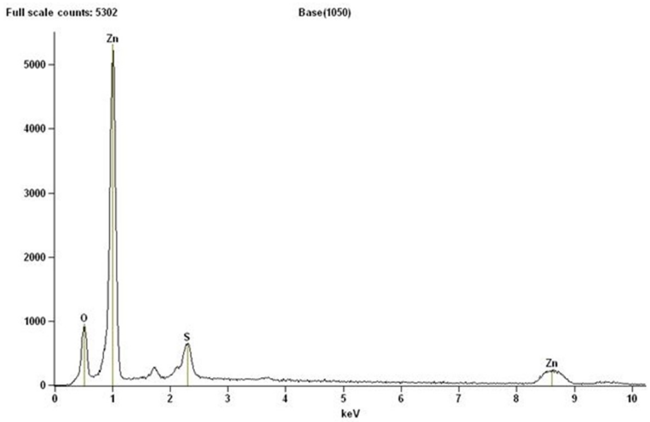

Figure 2. EDX analysis of Sample L_3

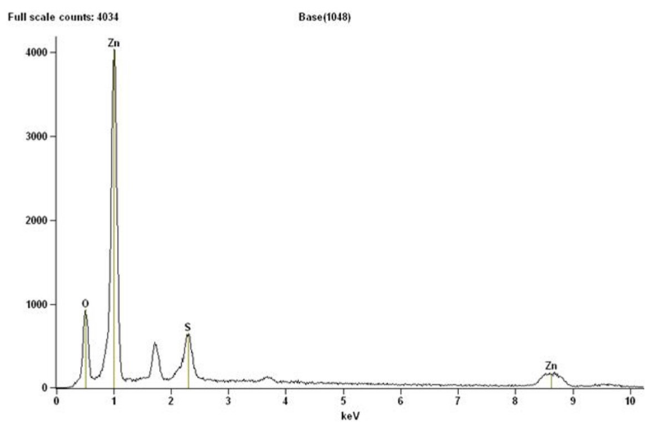

Figure 3. EDX analysis of sample L_9

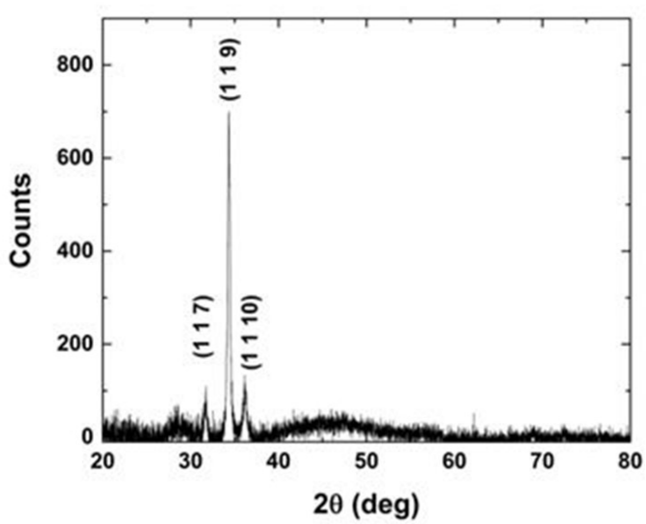

Figure 4. X-ray diffraction pattern of ZnS thin films

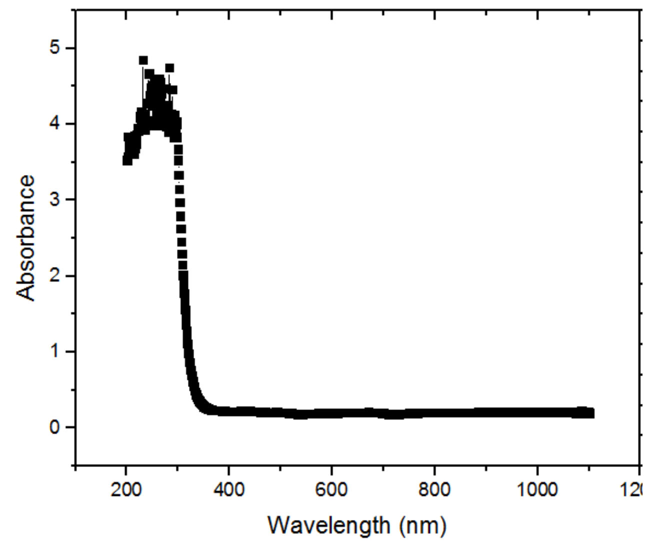

Figure 5. Absorption Spectra of ZnS nano particle

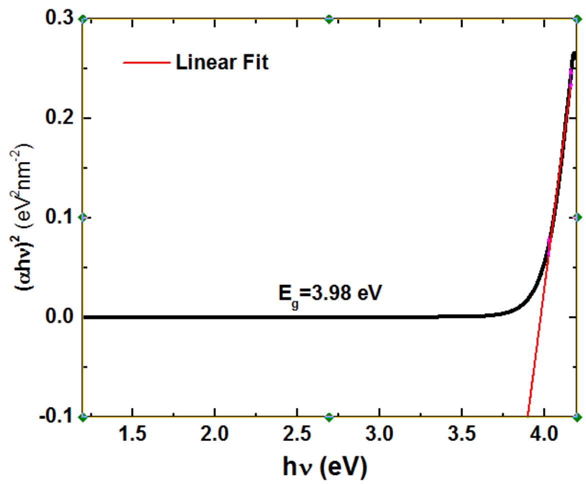

Figure 6. Tauc Plot

observed at the diffraction angle of 23.5° corresponding to the cubic (111) planes and hexagonal (002) planes. The average nano crystalline size (D) can be calculated using Debye – Scherrer formula:

$$D = 0.9\ \lambda / \beta \cos\theta$$

Where λ is the X-ray wavelength, θ is the Bragg diffraction angle, β corresponds to the FWHM of the XRD peak appearing at an angle θ. The average crystallite size found using Debye –Scherrer formula was 13.3nm.

3.3. Optical properties

The Optical properties of thin films were determined using UV-Vis Spectrometer in the wavelength range of 200 - 1100nm.Transmittance of ZnS thin films decreased with the increase of Zinc concentration in the thin films which may be due to the roughness of the films deposited. The thin films deposited at

0.025 M had high transparency due to low zinc concentration. This shows that the transmittance of ZnS thin films largely depend on the concentration of Zinc ions. Annealed ZnS samples also show a smooth absorption curve due the homogeneous nature of the film with less defects density. Annealing process increases the value of absorption coefficient and the fundamental absorption edge is shifted towards the higher values of photon energy which is due to the better crystalline nature of thin films.Fig 5. Shows the absorption spectra of ZnS thin film measured using UV-vis spectrometer. The absorption peak of nano particles, occurs in the range of 240-260nm clearly showing the widening of band gap. The Tauc relation can be used to calculate the band gap of ZnS thin films.

$$\alpha h\nu = A\left(h\nu - E_g\right)^{\frac{1}{r}}$$

where E_g is the band gap and r= ½ for direct allowed transitions. The band gap energy was determined by drawing the graph between $h\nu$ on the X axis and $(\alpha h\nu)^2$ on the Y axis and extrapolating the linear portion of the curve to the X axis which gives the energy of the material which is 3.98eVas shown in figure 6. This value is greater than the bulk ZnS (3.6 eV). This reveals that ZnS thin films investigated here show strong quantum refinement.Upon annealing, the band gap values as it reduces the secondary energy levels and the structure defects which leads to the contract tails region. This is the reason for the expansion in the band gap energy with increases with time and temperature of annealing.

4. CONCLUSIONS

ZnS thin films were coated using chemical bath deposition method by varying dipping time, solution concentration and annealing temperature. As coated samples were amorphous in nature and upon annealing, they transformed to poly crystalline films. The Band gap energy is found to increase with increase in Zinc concentration and also upon annealing. The Optimum parameters for coating the zinc Sulphide thin films were found as 90 min dipping time, 0.025 concentration of $ZnSO_4$ and 200°C annealing temperature which yields high band gap value of 3.98eV. The thin films can be used in the preparation of Solar cell applications.

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