International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.12 No.04, pp 219-225, 2019

Influence of Concentration and Annealing on the Properties of Chemical Bath Deposited Zns Thin Films

V. Sathana[1]*, K. Venkatesan[2]

[1]Department of Physics, St. Joseph's college of Arts & Science, Cuddalore-607 001, India
[2]Department of Physics, Dr.M.G.R Educational and Research Institute, chennai - 600 095, India

Abstract : The Nanosized ZnS thin films were prepared by chemical bath deposition technique. Zinc Sulfide (ZnS) was an important semiconductor material with large band gap (Approx. 3.5eV), high refractive index (2.35 at 632nm), high effective dielectric constant (9 at 1MHz) and wide wavelength pass band (0.4-13 Micrometer). The XRD pattern was showed that the deposited ZnS thin films in cubic structure. The SEM micrographs reveals that substrates were well covered and with appreciable grain size. Comparing both high and low concentration thin film, the band gap decreases and the absorption increases for high concentration also the annealing temperature. While increasing the annealing temperature the optical property of transmission was increased due to the growth of the ZnS particles. The concentration of 0.3M transmission is 73% in the visible region which are suitable for thermal imaging systems.
Key words : Zinc sulfide (ZnS), CBD, Concentration, Heat-treatment.

1. Introduction

Chemical bath deposition is a well-known deposition technique. They are mainly used for some Chalcogenides such as Zn, Co, Cd, Hg, Pb, Sulphides and selenides[1]. The thin films have mechanical, electrical, magnetic and optical properties which may differ from those of the bulk material and are used commonly in the form of a deposit on a suitable substrate for integrated circuits, resistors, capacitors, transistors and superconductors to name some [2].

The optical properties of these compounds made them useful as a filter, reflector and planar wave guide[3]. It has a vast potential for various application usage in optoelectronics and electroluminescent devices[4], antireflection coating for the solar cell[5.6], Blue light emitting laser diodes[7]. It can be used as α - particle detector[8].

DOI= http://dx.doi.org/10.20902/IJCTR.2019.120427

ZnS thin film is an n-type semiconductor with a wide direct band gap. The chemical bath deposition (CBD) technique was used to prepare the ZnS thin films[9,10,11]. Since it is a simple method, relatively less expensive and convenient for large area deposition. In our present work, the effect of varying the preparative parameters like concentration and annealing temperature on deposition process has been reported.

2. Experimental procedure

The solutions were prepared using analytical-grade reagents of $ZnSO_4$, thiourea and ammonia. The procedure involved that $ZnSO_4$ with concentration (0.2 M and 0.3 M) of 20 ml was taken in 100 ml beaker and stirred in the chemical bath for 1 hour (maximum) at 40 ^oC. The clear solution of ammonia (NH_3) was prepared and added from drop by drop to the $ZnSO_4$ solution to maintain the pH value up to 11 at 60 ^oC. Here ammonia will be the complexing reagent. Then 20 ml of thiourea solution with 0.2 M concentration was added from drop by drop at 80 ^oC to the chemical bath containing the $ZnSO_4$ and NH_3 solution. The constant stirring was continued in the chemical bath until the solution turned to ash color. Further solutions were prepared with various concentrations like (0.2 and 0.3) with constant pH value. The treated substrate was vertically immersed into the prepared chemical bath solution and the films were grown on the side facing the outside of the beaker was used for analysis. Beaker loaded with the zinc sulfide bath solution and substrate was held at a temperature selected in the range from 60 ^oC – 80 ^oC. On removal from the bath solution after the 3 hour, the coated substrate was either rinsed or sonicated in DI water before dried in air. After the deposition ultra-thin, color and very adherent ZnS films were observed.

3. Result and Discussion

3.1 Structural parameters

Zinc sulfide exists in sphalerite, cubic and hexagonal forms. Fig. 1 shows the X-ray diffraction patterns of polycrystalline ZnS films deposited at different concentration ranging from 0.2 M to 0.3 M. At concentration 0.3 M no diffraction peak is discernable that indicates highly disordered layer. Broad peaks corresponding to improved crystallinity start to appear, while the concentration decreases from 0.3 M to 0.2 M. One main peak can be observed at the diffraction angle of 28.8^o on the XRD spectrum obtained on the ZnS films prepared at concentration 0.2M. This peak is assigned to both cubic and hexagonal phases of the planes (111) ^{cub}/ (002) ^{hex}. Therefore, it can be concluded that we have prepared ZnS films having cubic structure whatever the tested concentration.

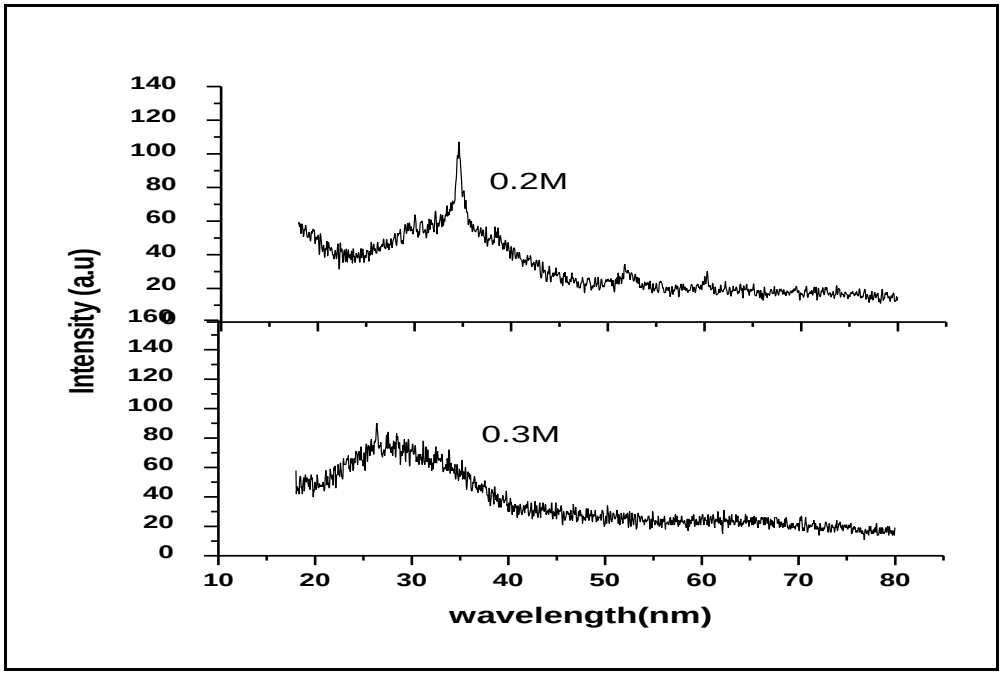

Fig: 1. X-ray diffraction patterns of ZnS thin films deposited on glass substrates at different concentration

The 0.2 M concentration sample was annealed at different temperatures like 300 ^{o}C and 500 ^{o}C for 2 hours. The X-ray diffraction of annealed sample were showed in Fig.2. The crystalline nature was improved by increasing the annealing temperature at 500 ^{o}C. In that 500 ^{o}C annealed sample was obtained the ZnS prominent diffraction peak compare to other conditions. The crystallite size 50 ~70 nm was calculated by the prominent diffraction peak using the Scherrer equation.

$$D = k\lambda/\beta\cos\theta \text{ ------ (1)}$$

Where, **D** is crystallite size, **k** is shape factor, λ is wavelength of the X-ray, **β** is Full width at Half Maximum (FWHM) of the diffracted pattern and **θ** is the corresponding diffraction angle. The diffraction peaks are matched with cubic structure and assigned the corresponding *(h k l)* values of *(1 1 1), (2 2 0) and (3 1 1)*.

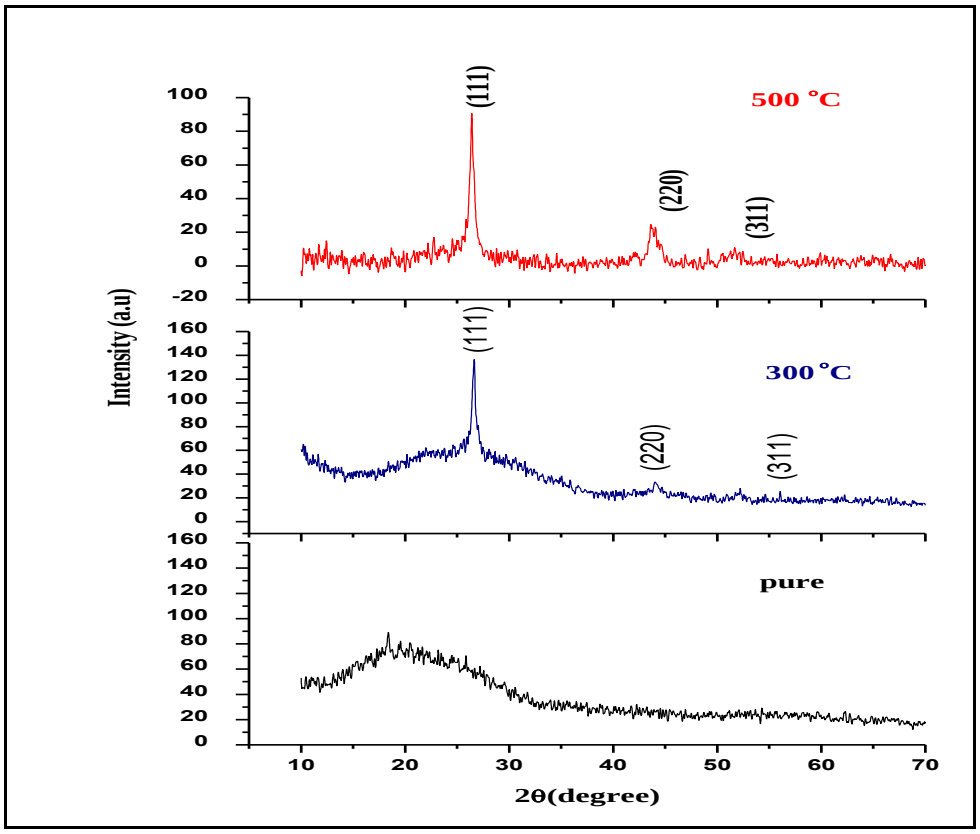

Fig: 2. **X-ray diffraction patterns of 0.2 M concentration ZnS thin films annealed at different temperature**

3.2 Optical Properties

The optical properties of ZnS thin film is determined from absorbance measurement in the range 300-900 nm Fig.3 shows the absorbance spectra of ZnS thin film. Absorbance coefficient α associated the strong absorption region of the film was calculated from absorbance (A) and the film thickness (t) using relation α = 2.3026 A/t The absorption coefficient α was analyzed using the following expression for optical absorption of semiconductors

$$(\alpha h\upsilon) = K\,(h\upsilon - Eg)^{n/2} \text{ ------- (2)}$$

Where, K is Boltzmann's constant, Eg is separation between valence and conduction bands and n is constant that is equal to 1 for direct band gap semiconductor.

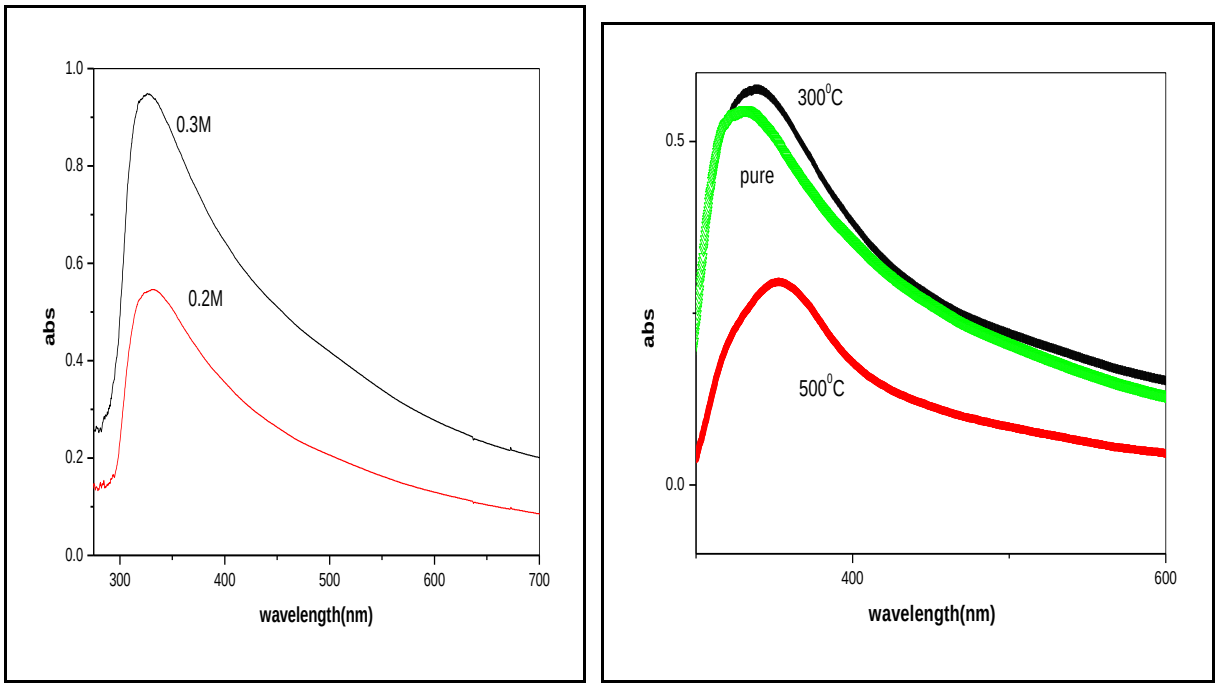

Fig: 3. Absorbance spectra of deposited for 0.2 M, 0.3 M and annealed sample of 0.2 M concentration

Transmission measurements are performed at normal incidence over a large spectral range (300 to 900 nm). The transmission spectra of ZnS thin films obtained at different concentration are displayed in Fig.4.

An increase of the transmission values over the whole spectral range is observed with increasing concentration values. In the transparency region, the largest transmission at 0.2 M concentration of sample annealed at 500 was observed with 99%. While increasing the annealing temperature the optical property of transmission was increased due to the growth of the ZnS particles. The concentration of 0.3M transmission is 73% in the visible region provides the comparably good transmittance that are suitable for thermal imaging systems [12,13]. Its unique combination of wide bandgap, allowing transmission of visible light, low-energy fundamental, phonon modes, allowing transmission in the long-wave infrared atmospheric transmission window (8–12 mm wavelength), and reasonable flexural strength have promoted its use as an infrared window material for thermal imaging[14]. However there was no detectable variation of the short wavelength absorption edge with the concentration.

To summarize, for the same deposition time, films grown at low growth rate (con=0.3M) are thinner and have lower absorption, whereas, films grown at higher growth rate (con=0.2M) are thicker and have higher absorption table 1 shows the Band gap values of the ZnS thin films for different concentration of the chemical bath.

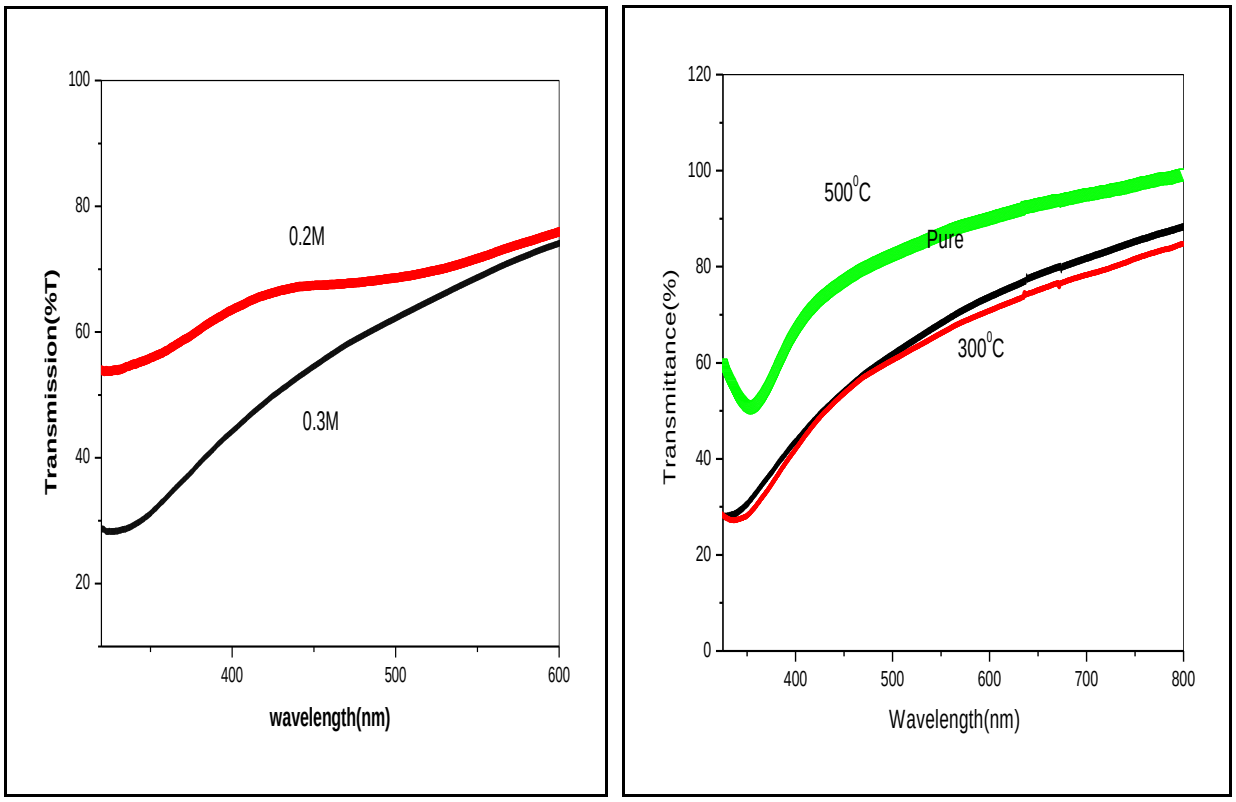

Fig: 4. Transmission spectra of as deposited 0.2 M, 0.3 M and annealed of 0.2 M concentration

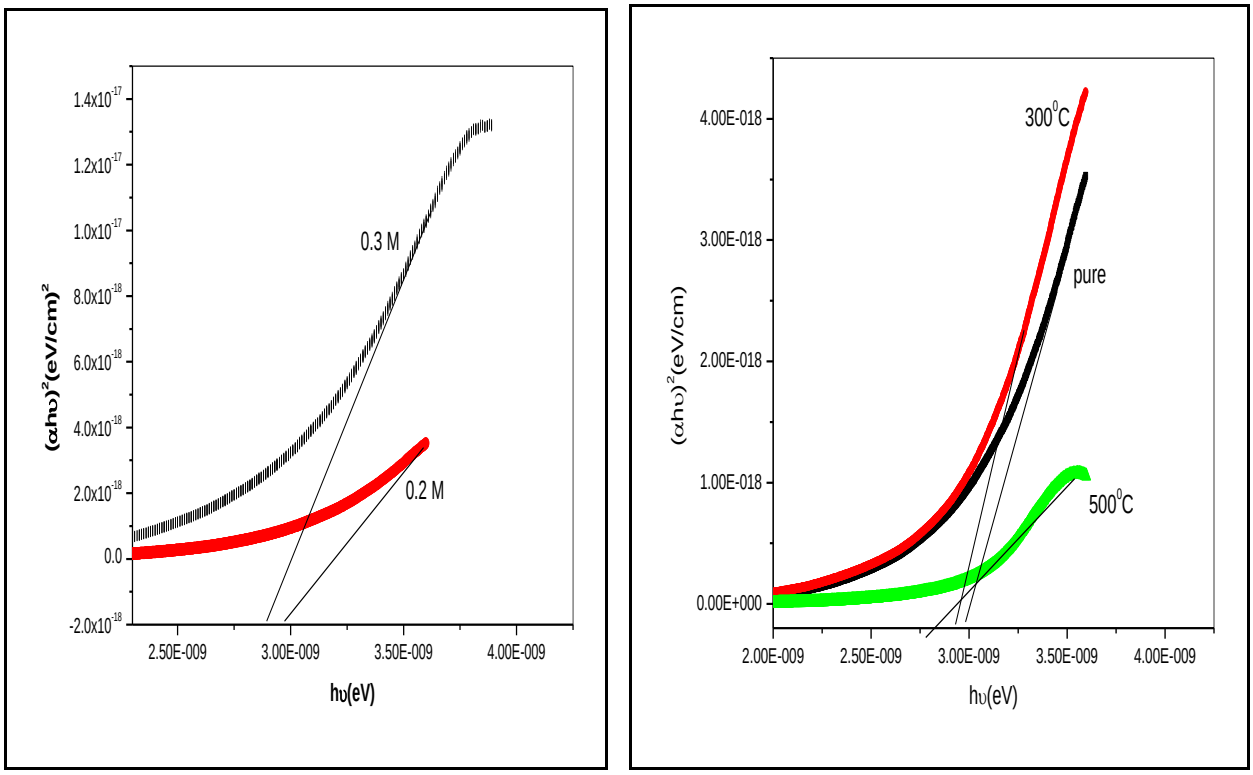

Fig: 5. Band gap for 0.2M, 0.3M and annealed sample of 0.2M concentration

The band gap was determined from the intersect of straight line portion of $(\alpha h\upsilon)^2$ versus $h\upsilon$ graph shown in fig. 5. The observed band gap values of the films for con 0.2M was 2.973eV and the band gap value for con 0.3M was 2.886 eV.

Table: 1. Band gap values for different concentration 0.2 M and 0.3 M

ZnS films prepared	Optical band gap (eV)
Concentration 0.2 M	2.973
Concentration 0.3 M	2.886

The band gap was obtained by extrapolating the straight portion of the curve to zero absorption coefficients. The band gap was calculated from the Fig. 5. The band gap of 0.2 M concentration was decreased with increasing the annealing temperature. The determined band gap values were tabulated in Table 2.

Table: 2. Band gap values for annealed ZnS samples

S.NO	ZnS FILM prepared condition	Optical band gap (eV)
1.	PURE	2.979
2.	ZnS_{300}	2.92
3.	ZnS_{500}	2.83

3.3 Surface morphology

SEM brings microscopic information of the surface structure and roughness. In this work, it appears to be a helpful technique to specify the growth mode via the study of a surface roughness, and to determine the effect of the concentration on the film morphology. Fig. 6. Shows Surface Topography of ZnS layers obtained at two different concentrations. Semispherical grains are uniformly distributed at the surface.

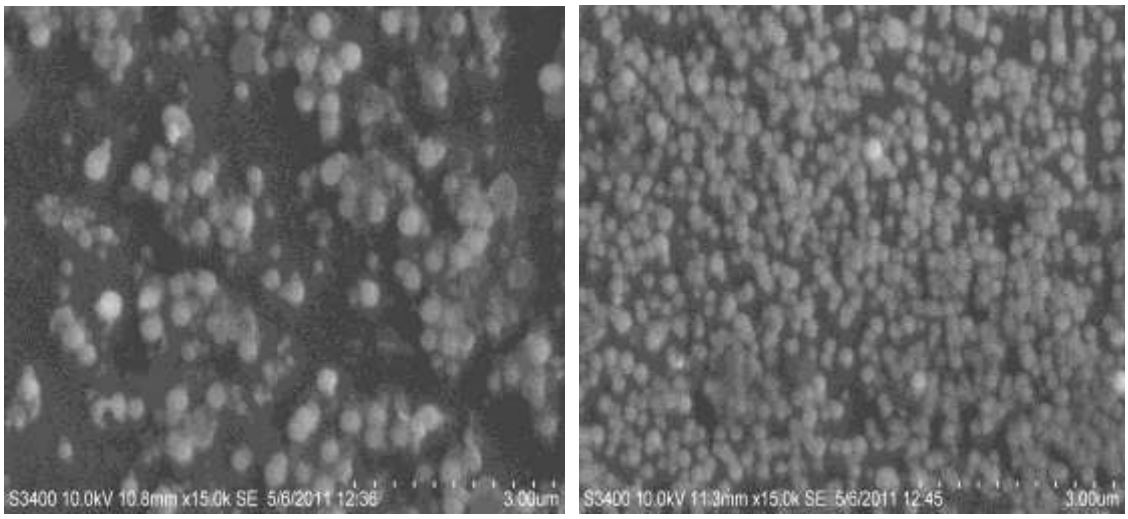

Fig: 6. SEM image of 0.3 and annealed sample of 0.2 M concentration

A slight increase in the concentration increasing the grain sizes and are more agglomerated. Concerning the nucleation stage film growth proceeds by nucleation of crystallites and then forming grains which coalesce to cover the entire substrate surface and to show a dense structure. The sphere type of morphology was observed at 0.2 M and 0.3 M concentration. The annealed sample was enhanced the distribution of ZnS particles on the glass substrate in the uniformity. The sphere was showed the particles were present in the nanosized level.

Conclusion

A simple Chemical Bath Deposition (CBD) technique was used for preparation of ZnS thin films on glass substrate. The XRD pattern showed that the deposited ZnS thin film is cubic structure. The crystallite size 50 ~ 70 nm was measured from the XRD diffraction prominent peak using Scherrer equation. The SEM micrographs reveals that substrate was well covered and with appreciable shape and grain size. Comparing both

high and low concentration thin film, the band gap decreases and the absorption increases for high concentration. Hence we conclude that we can produce the improved, compact and a granular straight with the minimum grain size by stimulating the concentration and annealing temperature. The band gap value of the deposited film is about 2.973 eV. Increase in annealing temperature and concentration of ZnS possess a good transmittance of about 73 % which is greater than that of subsequent hot isostatic pressed ZnS.

Reference

1. R.S. Mane, C.D. Lokhande, Chemical deposition method for metal chalcogenide thin films, Materials Chem & Phys. 65, 2000, 1-31.
2. G Hammond, Concise Dictionary of Physics and Related Subjects (2nd edn), Phys. Bull. 1979, 30 532 .
3. Mach R and Muller G O, Physics of electroluminescence devices, Journal of Luminescence, 1988, 40–41, 92-96.
4. Mika P valkonen , Seppo Lindroos , Roland Resch Markku Leskelä, Gernot Friedbacher, Manfred Grasserbauer, Growth of zinc sulfide thin films on (100)Si with the successive ionic layer adsorption and reaction method studied by atomic force microscopy, Applied Surface Science, 1998, 136, 1–2, 131-136.
5. Bloss, W.H. & Pfisterer, F & Schock, Hans-Werner. Advances in solar energy, an annual review of research and development. Am Sol Energy Soc Inc. 1998, 4.
6. Seung Wook Shin, So Ra Kang, Jae Ho Yun, A.V. Moholkar, Jong-Ha Moon, Jeong Yong Lee, Jin Hyeok Kim, Effect of different annealing conditions on the properties of chemically deposited ZnS thin films on ITO coated glass substrates, Solar Energy Materials & Solar Cells, 2011, 95, 856–863
7. Hasse, H.A., Qui, J., Depuydt, J.M., and Cheng, H. Blue-green laser diodes, Appl.Phys, Lett. 1991, 59:1272.
8. Kashani, H. Production and evaluation of ZnS thin films by the MOCVD technique as alpha-particle detectors, Thin Solid Films. 1996, 288(1-2),.
9. A.Cottrell, introduction to Mettallurgy , 1975, P.173
10. R.S.Longhurst, Geometrical & physical optics ,Longmans green,Londan 1957
11. Vipin Kumar , K.L.A. Khan ,G. Singh and T.P. Sharma , ZnSe sintered films: growth and characterization, Appl .Surf. Sci., 2007, 7, 253.
12. Zhang, Y., Chen, Y., Fu, X., & Luo, C, The research on the effect of atmospheric transmittance for the measuring accuracy of infrared thermal imager, Infrared Physics & Technology, 2016, 77, 375–381.
13. Gao, M., Tan, A., Zhang, B., Wang, L., Li, S., Chang, Q., & Peng, C. Design and realization of high resolution optical micro-scanning thermal microscope imaging system, Infrared Physics & Technology, 2018, 95, 46–52.
14. Wu, S., Zhao, J., Zhao, Y., Wang, K., Yang, W., Cheng, Haijuan Cheng, Rujie Li, Jie Jiang, Maozhong Li. Preparation, composition, and mechanical properties of CVD polycrystalline ZnS Infrared Physics & Technology, 2019, 98, 23-26.

*****