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Effect of growth temperature on structural and optical properties of hydrothermally grown ZnS thin films

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Abstract: The chemical bath deposition method was used for the preparation of ZnS thin films and their optical and structural properties were studied. The ZnS thin films were grown on well cleaned glass substrates by hydro thermal method 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. Effect of growth temperature on structural and optical properties was reported.

Keywords: ZnS, Hydro thermal, Growth temperature structural and optical properties.

I. Introduction and Experimental

ZnS is an important II-VI compound semiconductor with wide band gap energy of 3.7eV, has attracted much research interest due to its excellent properties in luminescence and photochemistry. ZnS is used in a variety of applications, including optical coatings, solid-state solar cell windows, in thin film electroluminescent devices [1], photoconductors, field effect transistors, sensors, and light-emitting applications [2]. ZnS thin films have been produced using various techniques such as thermal evaporation [3], molecular beam epitaxy [4], metal-organic vapor phase epitaxy [5], chemical vapor deposition [6], spray pyrolysis [7], RF reactive sputtering [8], Screen printing technique [9] and chemical bath deposition (CBD) [10]. Among them, chemical bath deposition is the commonly used method for production of ZnS layers.

In the present work, ZnS thin films have been prepared using chemical bath deposition method. The ZnS thin films deposited on substrate using hydrothermal process were characterized by using X-ray diffraction (XRD), UV-Visible spectroscopy and Photoluminescence (PL) spectroscopy.

Fig (1) shows the flow diagram of dip coated ZnS thin films deposited at 85°C and 150°C. ZnS films were prepared using a dip coating method. The Zinc Sulphate solution was prepared by adding Zinc Sulphate (ZnSO₄·7H₂O) with the de-ionized water and this mixture was stirred with magnet for 20 minutes.

Then Ammonia was added as a complexing agent on this ZnSO_4 solution drop by drop and solution was stirred continuously around 80 minutes. Thiourea solution was prepared by adding it with the de-ionized water and this mixture was stirred with magnet for 60 minutes.

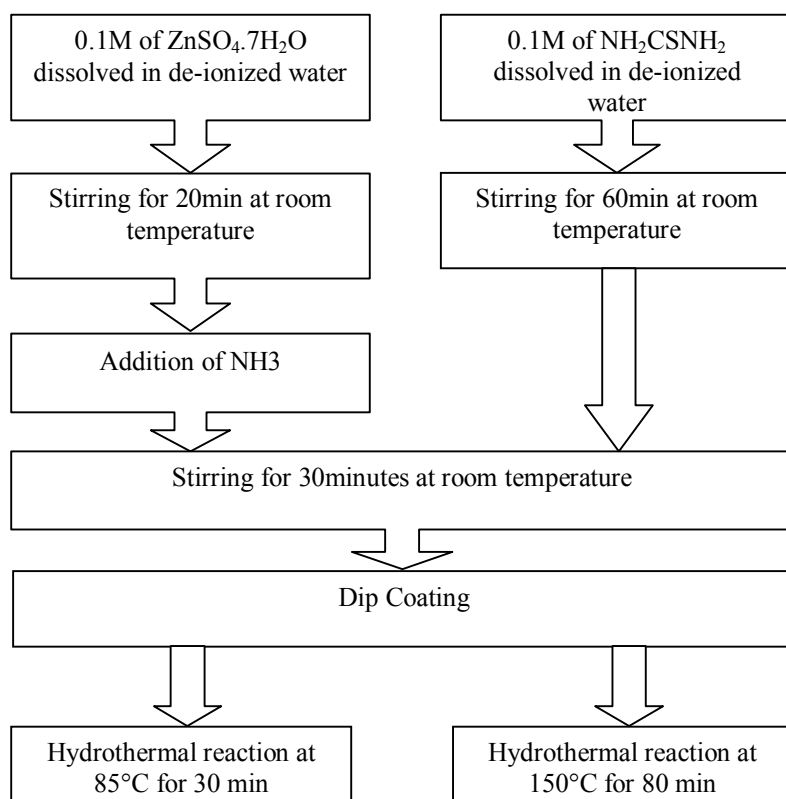


Fig (1) – Flow diagram of dip coated ZnS films at 85°C and 150°C

In the ZnSO_4 prepared solution, Thiourea solution was added drop by drop and continuously stirred this mixture with the magnet for 30 minutes. A set of well cleaned substrates were dipped into that final solution at two different temperatures i.e. 85°C and 150°C.

The structural characterization of the films was carried out using X-ray diffractometer with $\text{CuK}\alpha$ radiation ($\lambda=1.5404\text{\AA}$) in 2θ range from 10° to 80° . The optical properties like absorption and transmission spectra were taken using a UV spectrophotometer in the range 100 to 1600 nm. Photoluminescence (PL) spectra were recorded using luminescence spectrometer.

II. Results and Discussion

1. Structural properties

Fig (2) shows the XRD patterns of the obtained ZnS sample at 85°C & 150°C. The patterns (black coloured) of ZnS at 85°C show the lines at 14.35° and 21.49° which correspond [11] to (005) and (006) diffraction planes. As seen, the (005) peak has the strongest intensity. All the diffraction peaks could be indexed to hexagonal structure of ZnS (JCPDS: 72-0163).

The patterns (red coloured) of 150°C show the lines at 31.87° , 34.56° and 36.33° which correspond [12] to (104), (106) and (0010) diffraction planes. As seen, the (106) peak has the strongest intensity. All the diffraction peaks could be indexed to hexagonal structure of ZnS (JCPDS: 39-1363).

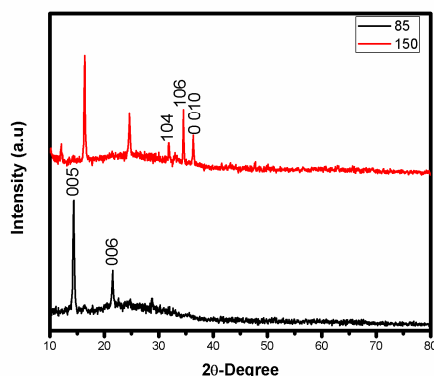


Fig (2) XRD patterns of ZnS thin films prepared at 85°C & 150°C

The XRD patterns clearly show the presence of ZnS, where all diffraction peaks is well indexed to the standard diffraction pattern of wurtzite-8H hexagonal ZnS phases. The average grain size of ZnS was estimated by using the well-known Scherrer's formula [13], $D = 0.94\lambda / \beta \cos\theta$ Where $\lambda = 1.5404\text{\AA}$ for $\text{CuK}\alpha$, β is the full width at half maximum (FWHM) of the peak corrected for the instrumental broadening in radians and θ is the Bragg's angle. The average grain size of ZnS thin films at 85°C and 150°C were found to be about 38 nm and 74 nm respectively.

2. Optical properties

To investigate the optical properties of the prepared ZnS thin films, UV-vis absorption spectra were recorded, as shown in fig (3). The optical absorption edge is approximately located at 286nm. An increase of the absorption values is observed with increase in deposition temperature. An estimation of the band gap value was obtained by the intersection point of the tangent of the absorption edge with the extended line of the diffuse reflection at lower wavelength. The obtained band gap value of ZnS films at 85°C and 150°C were found to be about 3.54eV nm and 3.49eV respectively, which compares favourably with the literature value for hexagonal ZnS, measured at room temperature, of 3.54eV [14].

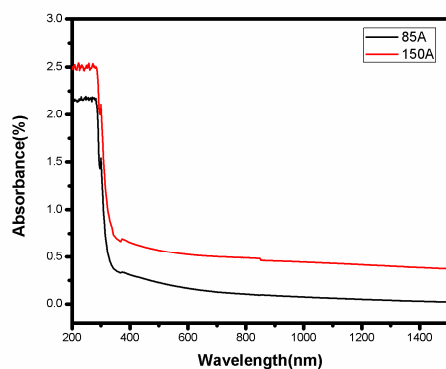


Fig (3)

Fig (3) UV-visible absorption spectra of ZnS thin films prepared at 85°C and 150°C;

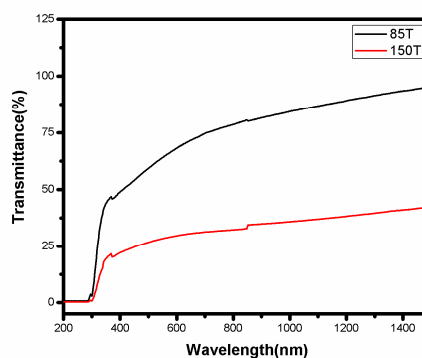


Fig (4)

Fig (4) Transmission spectra of ZnS thin films prepared at 85°C and 150°C

Transmission spectra of both ZnS thin films at 85°C and 150°C were depicted in fig (4). A decrease in the transmission values over the whole spectral range is observed with increase in deposition temperature.

Fig (5) shows the PL spectra of the samples prepared at 85°C and 150°C. The excitation wavelength is 295 nm in each case. PL peaks are found to be broad around 427 nm for ZnS film prepared at 150°C. The PL spectrum taken from the ZnS film prepared at 150°C depicts a strong intensity than ZnS film prepared at 85°C. ZnS film prepared at 85°C shows green emission (wavelength is around 500nm) and ZnS film prepared at 150°C shows violet emission (wavelength is around 427nm).

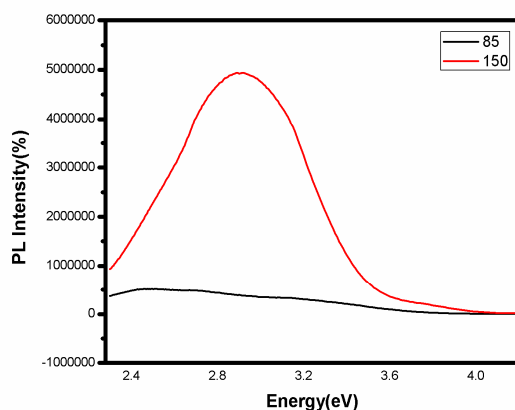


Fig (5) Photoluminescence spectra of ZnS thin films prepared at 85°C and 150°C

III. Conclusion

ZnS thin films were prepared on glass substrates by the CBD technique. The structure, optical properties and band gap of the samples were determined by XRD, UV-VIS and PL analyses. XRD analysis shows that the samples prepared were in a hexagonal phase. It was found that both structural and optical properties vary with deposition temperatures i.e. 85°C and 150°C. From the results, it was clearly observed that ZnS film prepared at 150°C has good structural and optical properties than ZnS film prepared at 85°C. It is reported that ZnS film prepared at 150°C has good absorbance intensity and broad visible emission. It is suggested that prepared ZnS film can be used to fabricate solar cells.

IV. References

1. Wen-Hua, Z.; Jian-Lin, S.; Hang-Rong, C.; Zi-Le, H.; Dong-Sheng, Y. *Chem. Mater.* 2001, 13, 648.
2. Bhargava, R. N.; Gallagher, D.; Hong, X.; Nurmikko, A. *Phys. Rev. Lett.* 1994, 72, 416.
3. Z. Porada, E. Schabowska, *Thin Solid Films* 145 (1986) 75.
4. M. Yoneta, M. Ohishi, H. Saito, *J. Cryst. Growth* 127 (1993) 314.
5. A. Aboundi, M. Diblasio, D. Bouchara, *Phys. Rev., B* 50 (1994) 11677.
6. H. Kashani, *Thin Solid Films* 288 (1996) 50.
7. R.R. Chamberlin, J.S. Skarman, *J. Electrochem. Soc.* 113 (1966) 86.
8. L.-Z. Shaoi, K.-H. Chang, H.-L. Hwang, *Appl. Surf. Sci.*, 2003, 305, 212-213.
9. Y.S. Kim, S.J. Yun, *Appl. Surf. Sci.*, 2004, 105, 229.
10. P.K. Nair, M.T.S. Nair, *Semicond. Sci. Technol.* 7 (1992) 239.
11. JCPDS database, card #72-0163
12. JCPDS database, card #39-1363
13. Guinier, X-Ray diffraction, (1963) Freeman, San Francisco, CA, USA.
14. D. R. Lide and H. P. R. Frederikse, CRC Press, Boca Raton, FL, CRC Handbook of Chemistry and Physics, ed. 77th edn., 1996, pp. 12-94.
