



International Journal Of
**Recent Scientific
Research**

ISSN: 0976-3031

Volume: 6(11) November -2015

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THE OFFICIAL PUBLICATION OF
INTERNATIONAL JOURNAL OF RECENT SCIENTIFIC RESEARCH (IJRSR)
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RESEARCH ARTICLE

SYNTHESIS AND CHARACTERIZATION OF ZNS THIN FILMS BY SOL-GEL DIP AND SPIN COATING METHODS

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ARTICLE INFO

Article History:

Received 06th August, 2015
Received in revised form
14th September, 2015
Accepted 23rd October, 2015
Published online 28st November,
2015

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 dip and spin coating methods 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. Effects of deposition techniques on structural and optical properties were reported.

Key words

ZnS, Dip Coating, Spin Coating,
Structural & Optical properties.

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INTRODUCTION

ZnS is a commercially important II-VI semiconductor having wide band gap energy of 3.7eV, rendering it a very attractive material for several kinds of applications like optical coatings, solid-state solar cell windows, anti-reflecting coatings (J. H. Park, J. Y. Kim, B. D. Chin, Y. C. Kim, and O. O. Park, 2004), photoconductors, field effect transistors, sensors, and bioelectronics (E. Katz, and I. Willner, 2004). ZnS film can be used as a reflector and dielectric filter due to its high value of refractive index as well as high transmittance in visible region. ZnS thin films have been produced using various techniques such as thermal evaporation (Z. Porada and E. Schabowska, 1986), molecular beam epitaxy (M. Yoneta, M. Ohishi, H. Saito and J. Cryst, 1993), metal-organic vapor phase epitaxy (A. Aboundi, M. Diblasio and D. Bouchara, 1994), micro-wave irradiation (Yu Zhao, J.-M. Hong and J.-J. Zhu, 2004), spray pyrolysis (R.R. Chamberlin and J.S. Skarman, 1966), RF reactive sputtering (L.-Z. Shaoi, K.-H. Chang and H.-L. Hwang, 2003), Screen printing technique (Y.S. Kim and S.J. Yun, 2004) and chemical bath deposition (P.K. Nair and M.T.S. Nair, 1992). Among them, chemical bath deposition is the commonly used method for production of ZnS layers.

Sol-Gel technique has the advantage of being low cost efficient method of producing large area films. The most important advantage of sol-gel over conventional coating methods is the ability to tailor the microstructure of the deposited film. In the present work, ZnS thin films have been prepared using chemical bath deposition method. The ZnS thin films deposited on substrate using sol-gel dip and spin coating methods were characterized by using X-ray diffraction (XRD), UV Visible spectroscopy and Photoluminescence (PL) spectroscopy.

Experimental Details

ZnS films were prepared using dip and spin coating methods. The Zinc Sulphate solution was prepared by adding Zinc Sulphate (ZnSO₄.7H₂O) with the de-ionized water and this mixture was stirred with the magnet for 30 minutes. Then Ammonia was added as a complexing agent on this ZnSO₄ solution drop by drop and the solution was stirred continuously around 60 minutes. Thiourea solution was prepared by adding it with the de-ionized water and this mixture was stirred with magnet for 80 minutes.

In the ZnSO₄ prepared solution, Thiourea solution was added drop by drop and this mix was continuously stirred with the

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magnet for 60 minutes.

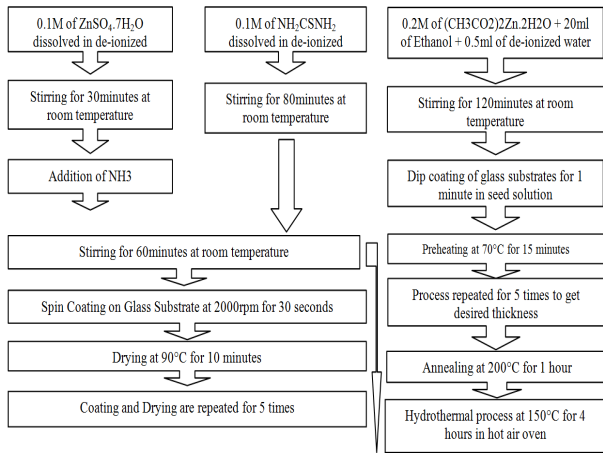


Fig 1 Flow diagram of sol-gel deposition process for dip and spin coated ZnS films

This solution was used to prepare spin and dip coated substrates. Spin coating was done on well cleaned substrates at 2000 rpm for 30 seconds and dried at 90°C per layer. Totally 5 layers were formed. Dip coating was done on seed layer substrates and these substrates were kept at 150°C in hot air oven for several hours. Seed layer substrates were prepared using Zinc Acetate dihydrate and ethanol. Fig (1) shows the flow diagram of dip and spin coated ZnS thin films.

RESULTS AND DISCUSSION

Structural properties

Fig (2) shows the XRD patterns of the obtained ZnS samples prepared using dip and spin coating methods. The detected (h k l) peaks of hydrothermally dip coated ZnS films (red coloured) were at 2θ values of 31.775°, 34.442° and 36.252° corresponding to the lattice planes (104), (106) and (0 0 10) respectively.

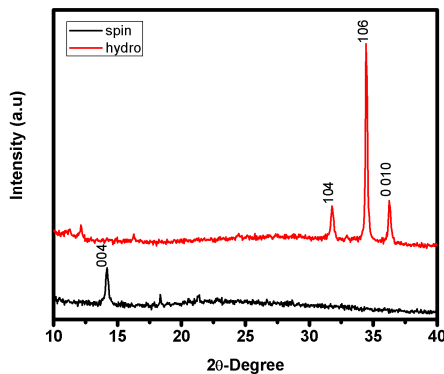


Fig 2 X-ray diffraction patterns of dip and spin coated ZnS films

As seen, the (106) peak has the strongest intensity. All the diffraction peaks could be indexed to hexagonal structure of ZnS (JCPDS: 39-1363). The XRD patterns (black coloured) of spin coated ZnS films show the peak at 14.174° which correspond to (004) diffraction plane. This peak could be indexed to hexagonal structure of ZnS (JCPDS: 72-0163). 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 (Guinier, 1963), $D = 0.94\lambda / \beta \cos\theta$ 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 dip and spin coated ZnS thin films were found to be about 70 nm and 38 nm respectively.

Optical properties

To investigate the optical properties of the prepared ZnS thin films, UV-vis absorption spectra were recorded, as shown in fig (3). An increase of the absorption values is observed with dip coated ZnS thin films than spin coated films. An estimation of the band gap value was obtained by the intersection point of the tangent of the absorption edge. The obtained band gap value of dip and spin coated ZnS films were found to be about 3.724eV and 3.68eV respectively, which closely agree with the values reported for ZnS thin films obtained by CBD (J.M. Dona and J. Herrero, 1994, T. Nakada, M. Mizutani, Y. Hagiwara and A. Kunioka, 2001).

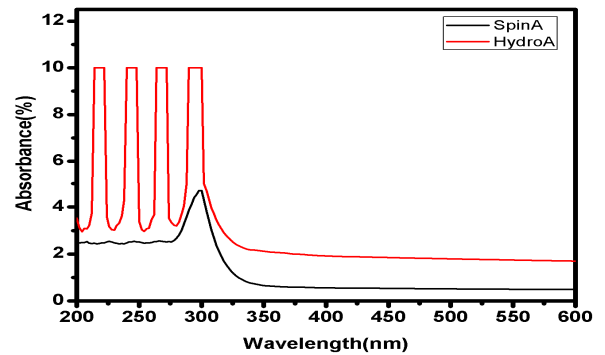


Fig 3 UV-visible absorption spectra of the dip and spin coated ZnS films

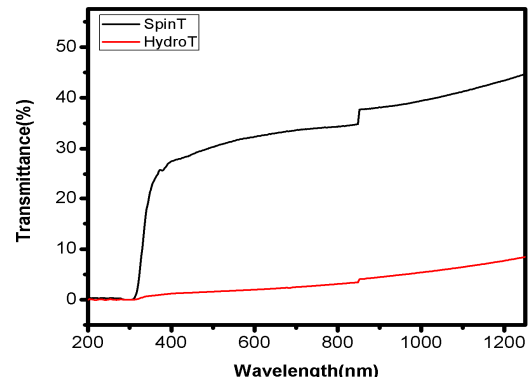


Fig 4 Transmittance spectra of dip and spin coated ZnS films

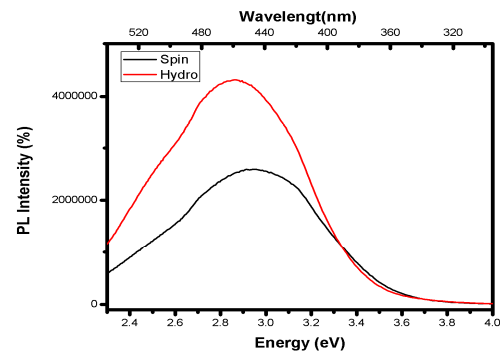


Fig 5 Photoluminescence spectra of dip and spin coated ZnS film

Transmission spectra of both dip and spin coated ZnS thin films were depicted in fig (4). A decrease in the transmission

values over the whole spectral range is observed with dip coated ZnS film compared to spin coated film. Fig (5) shows the PL spectra of the samples prepared by dip and spin coating methods. The excitation wavelength is 345 nm in each case. For PL peaks are found to be broad around 458 nm dip coated ZnS film. The PL spectrum taken from the dip coated ZnS film depicts a strong intensity than spin coated ZnS film. Both dip and spin coated ZnS film shows indigo emission (wavelength is around 458nm & 448nm respectively).

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. The average grain size of dip and spin coated ZnS thin films were found to be about 70 nm and 38 nm respectively. UV results show that absorbance of dip coated ZnS thin film is better than spin coated ZnS film and vice-versa for transmittance. The obtained band gap value of dip and spin coated ZnS films were found to be about 3.724eV and 3.68eV respectively. The PL spectra shows that both dip and spin coated ZnS thin films have indigo emission. It was found that both structural and optical properties vary with coating techniques i.e. dip and spin coating. From the results, it was clearly observed that dip coated ZnS film has good structural and optical properties than spin coated ZnS film. It is reported that dip coated ZnS film has good absorbance intensity and broad visible emission. It is suggested that prepared ZnS thin films can be used to fabricate solar cells.

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How to cite this article:

Kumar V *et al.*, Synthesis And Characterization Of Zns Thin Films By Sol-Gel Dip And Spin Coating Methods. *International Journal of Recent Scientific Research Vol. 6, Issue, 11, pp. 7377-7379, November, 2015*

ISSN 0976-3031



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