Optical and Structural Properties of ZnS Thin Films Grown by Chemical Bath Deposition Technique using two different Zinc Salts

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Abstract—*Semiconducting zinc sulphide (ZnS) thin films of the II-VI group is a promising alternative buffer layer for substituting the toxic CdS material, have been deposited on glass substrate using two different zinc salts by chemical bath deposition technique at the same preparative conditions and study the effect of two zinc salts on the properties of the films .The zinc precursors used were zinc acetate and zinc sulfate. The compositional, morphological, structural and optical analysis of the samples were characterized by X-ray diffraction (XRD), X-ray energy dispersive spectroscopy(EDAX), scanning electron microscopy(SEM), photoluminescence (PL) and UV-Visible spectroscopy were used . X-ray diffraction (XRD) patterns of ZnS thin films prove disordered and amorphous nature of the surface of ZnS thin films since it does not revealing any peaks. SEM and EDAX micrographs reveal that the surface of as synthesized ZnS thin film grown from $ZnSO_4$ is more uniform and stoichiometric than grown from $Zn(CH_3COO)_2$. UV spectroscopy studies show good transmission characteristic with an average transmittance of 80-90% for both the films and direct band gap of deposited films are in the range of 3.75 eV to 3.80 eV. Photoluminescence spectrum shows three emission peaks, the dominant peak lies at 540nm and the low intensity blue peaks lie at 450 nm and 468 nm .*

1. INTRODUCTION

Zinc sulfide (ZnS), a direct and wide band-gap semiconductor (Eg~ 3.7 eV) which crystallizes in both cubic and hexagonal forms, has been extensively investigated for the past decades as it has numerous applications in the fabrication of optoelectronic devices such as in blue light emitting diodes, electroluminescent devices, flat panel displays, sensors, lasers and n-window layers for thin film heterojunction solar cells, photoconductor and especially photovoltaic devices[1,2].Recently thin films of ZnS have been successfully used as buffer layers to replace the CdS used in CIGS based solar cells and has achieved a maximum efficiency of 18.6% [3]. Although, CdS is the most promising buffer layer for thin film heterojunction solar cells but there are related environmental concerns due to the large amount of cadmium-containing waste produced in the fabrication process of CdS by CBD technique [4]. The main advantages of using ZnS are (i) ZnS is less toxic than CdS, (ii) its wider energy band gap (3.7eV) allows transmission of more high-energy photons to the junction than CdS (energy bandgap,2.42eV) enhancing the blue response of devices[5]. Several growth techniques, such as CBD [6], metal organic chemical vapor deposition [7], molecular beam epitaxy [8], and atomic layer epitaxy [9], have been applied to grow high quality ZnS films for device applications in electroluminescent displays and solar cells. But among these methods, CBD is the most popular method because of its low cost, easy coating of smooth and uniform large surfaces, low deposition temperature and can be carried out at atmospheric pressure [2, 10].

2. EXPERIMENTAL

2.1 Materials and characterizing techniques

Zinc acetate [$Zn(CH_3COO)_2.2H_2O$], zinc sulphate [$ZnSO_4.7H_20$] thiourea [$CS(NH_2)_2$], tri-sodium citrate [$C_6H_5Na_3O_7.2H_2O$], were purchased from Merk (India)Ltd. and used directly as received. Deionized water was used throughout the experiments. The crystal structures of the films were analyzed by using a Rigaku Miniflex X-ray diffractometer with intense CuKα radiation (λ=0.154nm) .For optical studies, absorption and transmission spectra were recorded with Shimadzu UV-Vis spectrophotometer. Surface morphology of the films was examined by JSM 6360(JEOL) Scanning Electron Microscope (SEM) and composition of the films was obtained by energy-dispersive X-ray spectroscopy (EDS).

2.2 Synthesis of ZnS thin film.

ZnS thin films were deposited on glass substrates by chemical bath deposition using two different zinc salts. The substrates were cleaned with a soapy solution rinsed with distilled water and then with nitric acid followed by isopropanol, kept in an ultrasonic bath and finally rinsed with deionized water. Zinc acetate /Zinc sulphate, thiourea, ammonia and tri-sodium

citrate were used as the raw materials for the preparation of ZnS thin films. The films were prepared at the same preparative conditions such as bath temperature, deposition time and p^H etc. First of all 20ml of 0.8M solution of zinc acetate/ zinc sulphate and 10ml of 0.6M solution of tri-sodium citrate were mixed and stirred for 30 minutes. After that 20ml of 0.8M solution of thiourea was added slowly to the mixed solution under stirring condition. Finally a sufficient amount of ammonia was added to the solution so that its p^H should be adjusted at 10 and thereafter the solution was stirred for several minutes until it becomes clear and homogeneous. The pre-cleaned glass substrates were immersed vertically in the solution and placed in a water bath at 80^0C for three hours and then left it for 18 hours. After deposition the glass substrates were washed in running tap water, rinsed in deionized water and dried in air.

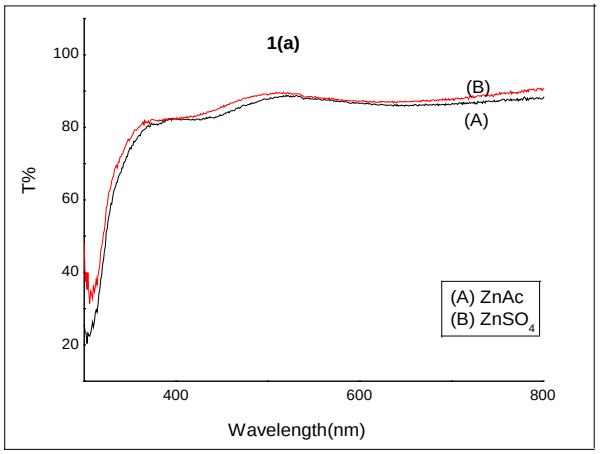
3. RESULTS AND DISCUSSION.

3.1 Optical Studies.

The UV- visible transmission spectra of as synthesized ZnS thin films deposited on glass substrate with two different zinc salts i.e. zinc acetate and zinc sulphate are shown in fig 1(a). From the spectra it is observed that both the films show an average transmission of 80-90% in the visible range. The optical band gaps of the films were obtained by using the following equation [11] for a semiconductor

$$\alpha = K (h\nu - Eg)^{m/2}/h\nu \qquad (1)$$

where 'α' is the absorbance, 'K' is a constant and 'm' is equal to '1' for direct transition and '2' for indirect transition.. The extrapolation of the straight line to $(\alpha h\nu)^2 = 0$ axis (Fig.1b) gives the energy band gap of the film material. The band gap of the ZnS film deposited using ZnAc had band gap energy of 3.75eV and that from using $ZnSO_4$ were found 3.79eV.



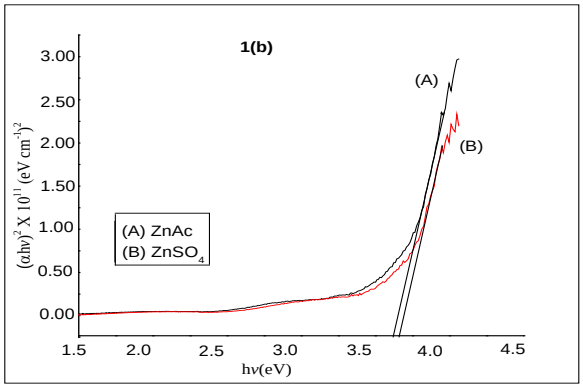


Fig. 1: (a). UV-Vis absorption spectra of ZnS thin films prepared using two different zinc salts; (b) band gap calculation of ZnS thin films prepared using two different zinc salts.

3.2. Morphology and stoichiometry

The SEM micrographs at two different magnifications for the ZnS thin film deposited by using two zinc salts are shown in Fig. 2. Low

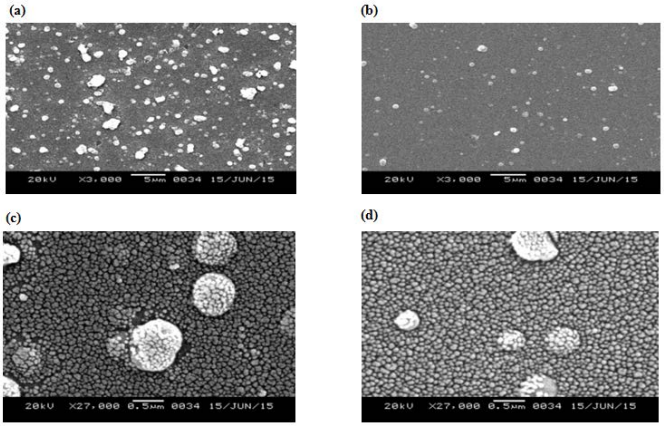


Fig. 2: SEM images of ZnS thin films at low magnification (a)ZnAc (b) ZnSO4 and at high magnification (c)ZnAc (d)ZnSO4

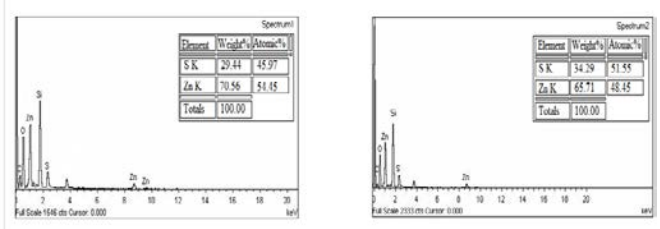


Fig3: Spectrum1- ZnS thin film grown from zinc acetate. Spectrum2- ZnS thin film grown from zinc sulphate.

magnification images (a) and (b) indicate that both the ZnS thin films are discontinuous with some ZnS clusters on the surface, but the cluster formation on the surface of ZnS film grown from $ZnSO_4$ is comparatively less than the film grown

from ZnAc. From the high magnification images of ZnS films indicate that the film deposited using $ZnSO_4$ [Fig. 2(d)] is free of pinholes. It is also observed from high magnification images that the film surface exhibits granular texture, with grains ranging from 80 to 100 nm. Fig 3 (a) and (b) shows the variation of Zn and S chemical compositions in ZnS films using two

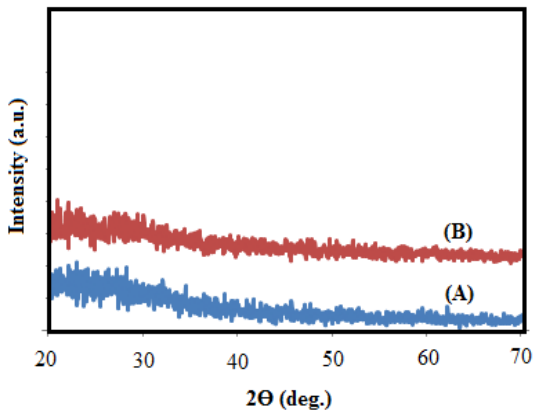


Fig4: XRD spectrum of ZnS thin films grown from (A) zinc acetate (B) zinc sulphate.

different zinc salts zinc acetate zinc sulphate respectively analyzed by EDS. The EDS analysis confirms the presence of zinc and sulphur in ZnS thin film. Both the samples prepared using two different zinc salts were non-stoichiometric. Zn has more content than S in the film grown from zinc acetate and its Zn/S ratio is 1.184. A slight excess of Zn may be caused by very small amount of $Zn(OH)_2$ or ZnO originated from the alkaline reaction solution [12]. On the other hand in the ZnS thin film grown from zinc sulphate has more S content than Zn with Zn/S ratio 0.93 which is nearly stoichiometric than the value 1.184. EDAX spectrum also shows that prepared films are free from impurities. The presence of silicon (Si) and oxygen (O) are due to glass substrates [13] and also T. Ben Nasr et al.reported that the presence of oxygen into the film may be from the atmosphere or from the aqueous medium of the bath solution [14].

3.3. Structural analysis.

Fig. 4 shows the XRD patterns of as-deposited ZnS thin films prepared using different zinc salts zinc acetate and zinc sulphate. The result does not show any discernable peaks corresponding to ZnS planes for the thin films deposited using ZnAc or $ZnSO_4$. This may be due to highly disordered amorphous nature of ZnS thin films as reported by previous groups [15,16,17] . Jun Liu et al. reported that low thicknesses of ZnS thin film did not exhibit any discernible peaks which is only possible by using multiple depositions technique to increase the thickness[3].

3.4 Photoluminescence (PL) Study.

Fig. 5 shows a typical PL spectrum of ZnS thin films deposited from two zinc salts under the 330 nm excitation. The PL spectrum is composed by three emission bands 450nm, 468nm and 542 nm.

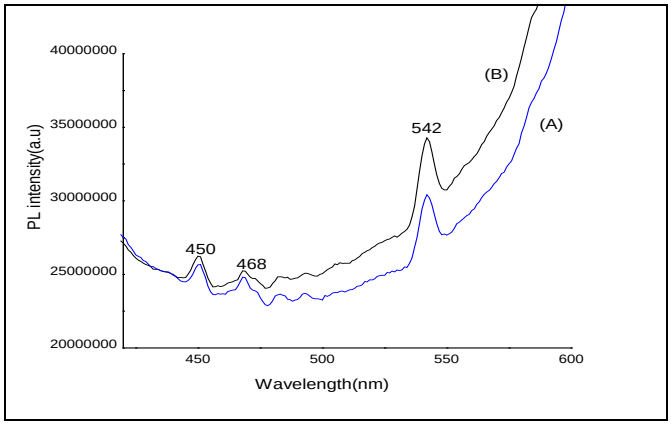


Fig. 5: PL spectrum of as synthesized ZnS thin film deposited from (A) zinc acetate (B)zinc sulphate

Both the ZnS films have similar peaks at same wavelengths. The violet-blue emission centered at450 and 468 nm may be ascribed to a transition involving vacancy states, which was suggested by Denzler et al. in ZnS nanocrystals and by Lee and co-workers in nanoribbons [18**].** The dominant peak at 540nm may be due to some other defects.

4. CONCLUSION

ZnS thin films were successfully deposited on glass substrates via the CBD technique using two different zinc salts and a non toxic complexing agent tri-sodium citrate. The effects of the different salts on the structure, composition, morphology, optical properties of the ZnS thin films were investigated. The ZnS thin films prepared using zinc acetate are composed of clusters and found zinc rich from EDS analysis. However, the ZnS thin films prepared using zinc sulphate are free from pinholes and composed of a large number of uniform grains of approximately 80-100 nm in size and nearly stoichiometric than prepared from zinc acetate. The optical band gap is found to be 3.79eV. PL spectrum for both the films indicates that they have similar kind of defects. The morphology and optical properties of the obtained ZnS film from zinc sulphate salt enable it to be used as window layers for solar cells.

5. ACKNOWLEDGEMENT

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