The studies on optical and structural properties of zinc sulfide thin films deposited by SILAR method

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ABSTRACT

In the present work, the compound semiconducting zinc sulfide (ZnS) thin films were deposited on glass substrate using successive ionic layer adsorption and reaction technique by the various sulfur concentration(0.2 M to 1 M). The preparative parameters such as concentration, temperature, deposition time, pH of solution have been optimized. The characterization of thin films was carried out for the structural and optical properties. The thin films were characterized by using X-ray diffraction (XRD), UV-VIS Spectra and photoluminescence (PL). The X-ray diffraction pattern (XRD) revealed that the ZnS film has hexagonal and cubic crystal structure. All deposited films exhibit a relatively high transparency in the range of 300 to 800 nm. The band gap varies from 3 to 3.75 eV. Photoluminescence spectra showed blue emission band (480 nm) and green emission band (524 nm).

Key words: zinc sulfide, absorption coefficient and photoluminescence (PL).
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INTRODUCTION

ZnS is one of the earliest semiconductors discovered and has novel fundamental property in order to suit diverged application. It is non toxic to human body and abundant. ZnS in its nano structures form attracted researches attention due to its special structure (Zinc blend and wurtzite) related to chemical and physical properties and for potential application in optoelectronic and nano electronic devices which includes blue LED's, electroluminescence, photoluminescence, cathodoluminescence, sensors, solar cells etc.[1]. In addition, Chalcopyrite-based thin film devices (CIGS) contain a so-called buffer layer, made of cadmium sulfide (CdS). Cadmium is highly toxic and therefore, alternative materials are being sought that can replace CdS without losses in its performance. The ZnS is an alternative to CdS [2-5]. Several techniques on growing ZnS thin film have been reported, which include sputtering[6], spray pyrolysis[7], chemical bath deposition[8,9], molecular beam epitaxy (MBE) [10], pulsed-laser deposition (PLD) [11], chemical vapour deposition (CVD) [12], metalorganic chemical vapour deposition (MOCVD) [13], metalorganic vapour-phase epitaxy (MOVPE) [13], atomic layer epitaxy (ALE) [14] and successive ionic layer adsorption and reaction (SILAR) [15]. Among these methods, the SILAR is relatively cost effect, simple and convenient for large area deposition which suit for doping different element in an easy way and which require any sophistication. In the present work, ZnS thin films were grown by SILAR technique through a different set of precursor. Different ZnS thin films were deposited by varying five different anion source concentrations and were characterized for their optical and structural properties.

EXPERIMENTAL SECTION

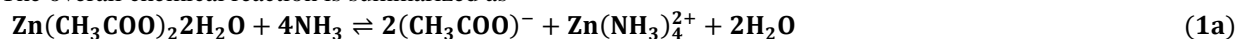*2.1Preparation and Substrate cleaning of ZnS thin films*
ZnS thin films were grown on glass substrates by the SILAR technique. To deposit ZnS one SILAR growth cycle involves the following four steps: a well-cleaned glass substrate is immersed in the first reaction vessel containing

aqueous cation precursor 0.2M Zinc acetate dehydrate solution at pH 10. After the cation immersion, the substrate is moved to the rinsing vessel where it is washed with purified water. The sulphide ions were adsorbed from an aqueous 0.2 M Thiourea solution with pH 12 which acts as anion source. After anion immersion the substrate was washed as described above; thus the first SILAR growth cycle is finished. Repeating these cycles a thin film with desired thickness can be grown. The cation and anion immersion times were 15 s. The temperature of the solutions was maintained at 65 °C (± 5°C). The ammonium hydroxide was used as complexing agent. The different thin films were prepared by varying the zinc to sulphide source ratio as 1:1, 2, 3, 4 and 5 respectively. The preparative parameters used for the deposition of ZnS thin films are summarized as below (Table 1). The glass slides of dimensions 26mm×76mm×2mm were used. Before deposition, they were etched by using chromic acid bath kept at 70^0c for 2h. After the etching process, they were cleaned with deionized water and acetone. The substrate cleaning plays an important role in the deposition of thin film. The cleaned substrate surface provides nucleation sites, which results in uniform film growth [16].

Table 1. ZnS thin film synthesis parameter.

S.NO.	PARAMETER	CATION SOULTION	ANION SOLUTION
1.	Materials	Zinc acetate dehydrate	Thiourea
2.	Concentration of solution	0.2 M	0.2, 0.4, 0.6, 0.8 and 1 M
3.	pH value	10	12
4.	Solution temperature	65°C	65°C
5.	Immersion time	15 s	15 s
6.	Total number of deposition cycles	100	100

The overall chemical reaction is summarized as

$$Zn(CH_3COO)_2 2H_2O + 4NH_3 \rightleftharpoons 2(CH_3COO)^- + Zn(NH_3)_4^{2+} + 2H_2O \tag{1a}$$

$$Zn(NH_3)_4^{2+} \rightleftharpoons Zn^{2+} + 4NH_3 \tag{1b}$$

$$SC(NH_2)_2 + 2OH^- \longrightarrow S^{2-} + CH_2N_2 + 2H_2O \tag{2}$$

$$Zn^{2+} + S^{2-} \longrightarrow ZnS \tag{3}$$

2.2 Characterization of thin films
The thickness of the sample was determined by the gravimetric method. The optical properties of ZnS thin films were calculated as a function of concentration of sulphide solution. The UltraViolet-Visible (UV-Vis) spectrophotograph was recorded using the PERKIN ELMER Lambda 35 spectrometer. As the films were examined along with the substrates on which they were formed, it was necessary to take into account the absorbance in the glass substrate even though it was small. Hence, the absorbance spectra of the glass substrates were taken and used for the elimination of the optical absorbance in the glass substrate from the total absorbance in the film–substrate combination to obtain the optical absorbance of the film. The band gap energy change was investigated as function of concentration of sulphide solution. Room temperature photoluminescence (PL) study was performed by using Varian Cary Eclipse fluorescence spectrophotometer. The samples were excited using the 385 nm line. The structure of the film was identified by X-ray diffraction (XRD) with XPERT-PRO (PW-3071) equipped with a Cu Kα (λ=0.154060 nm) radiation source. Data were collected by step scanning from 20^0 to 80^0 with step size of 0.05^0 (2θ).

RESULTS AND DISCUSSION

3.1 Optical characterization
The optical transmittance of as deposited ZnS thin film which deposited varies with respect to the sulphur concentration is shown below (Fig 1). The wavelength of the incident light is 220-1000nm. It reveals that nearly 85% transmittance in the visible wavelength range. In addition, the transmittance decreases at the Zn:S ratio of 1:5. It can be seen that the Zn:S ratio of 1:5 thin film has lower transparency, because it has thicker than the others. Moreover, this film was densely covered by particles and the space of the particle was less so the light cannot transmit easily. So the concentration of sulphur is very important to obtain the high quality ZnS thin film. The optical absorption spectrum of as deposited ZnS thin film varies with respect to the sulphur concentration is shown below (Fig 2). It is clearly seen from the spectra that the film has sharp absorption and the absorption edge slightly shifting towards the lower wavelength indicates the increase of optical band gap. The energy band gap of these thin films was determined from absorption spectra using Tauc's relation, [17]

$$\alpha = \frac{K}{h\nu}(h\nu - E_g)^n \tag{4}$$

Where K is a constant, hν is the photon energy, α is a absorption coefficient and n assumes values of 1/2, 2, 3/2 and 3 for allowed direct, allowed indirect and forbidden indirect transitions respectively. The value of the absorption coefficient 'α' has calculated using the relation, [18]

$$\alpha = \frac{2.3026\,A}{t} \tag{5}$$
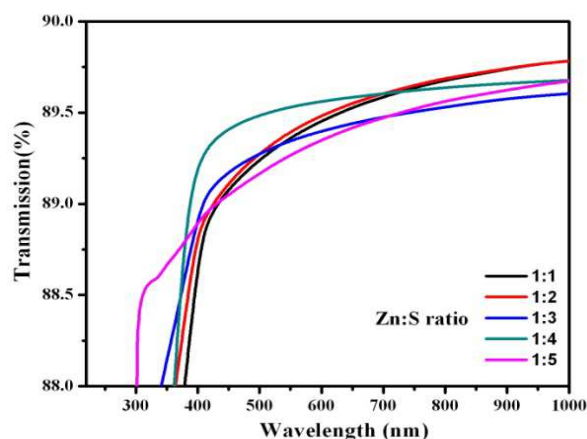
Where A is the absorbance and t is the film thickness.
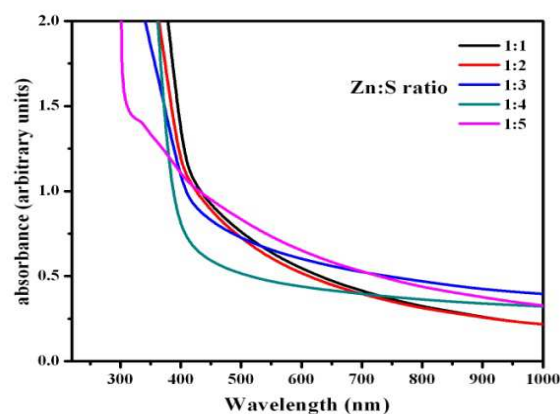

Fig. (1). Transmittance spectra of ZnS films

Fig. (2). Absorbance spectra of ZnS thin film

Thus a plot of α^2 vs. hν is a straight line whose intercept on the energy axis gives the energy gap, E_g. The variation of α^2 vs. hν for different sulphur concentration is as shown below (Fig 3). The band gap energies of thin film have been determined by the extrapolation of the linear region on the energy axis. The band gap energy in ZnS thin film is increasing with increasing sulphur concentration. The band gap energy varies from 3 eV to 3.75 eV. The extinction coefficient K_f value decreases with increase in wavelength and becomes constant at higher wavelength (Fig 4). The Extinction coefficients are calculated using the following equation (Equ 6). The extinction coefficient (K_f) is directly related to the absorption of light. In the case of polycrystalline films, extra absorption of light occurs at the grain boundaries [19-20]. This leads to non-zero value of (K) for photon energies smaller than the fundamental absorption edge [21-23].

$$K_f = \frac{\alpha\lambda}{4\pi} \tag{6}$$

3.2 Photoluminescence (PL) study
The room temperature Photoluminescence spectrum of ZnS thin films for various Zn:S ratios are shown in below (Fig 5). It can be seen that the emission is quite symmetric and sharp. There are mainly three luminescence bands present in the all the films, two blue emission band around 413 nm and 480 nm and one green emission band around 525 nm. The luminescence peaks located around 413 nm is associated with the zinc vacancies and that at 480 nm is probably due to sulphur vacancies [24-28]. The green luminescence peaks located around 524 nm is associated with oxide vacancies. It can be seen that as the concentration of sulphur increases the intensity of the emission decreases. The PL signal obtained is quite sensitive to the impurities of defect present within the sample. The decrease in intensity explains that the defect present in the sample also decreases. The emission might be arising from vacancy of sulphur which gets reduced with an increase in concentration of sulphur.
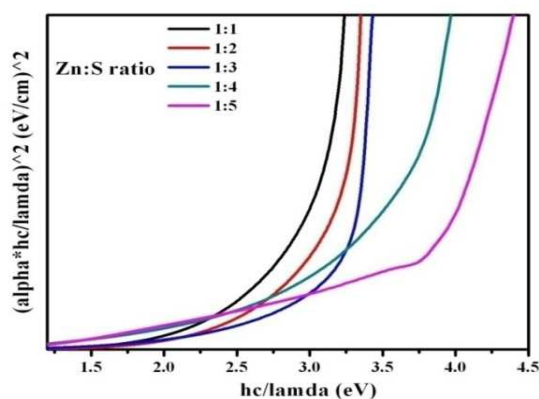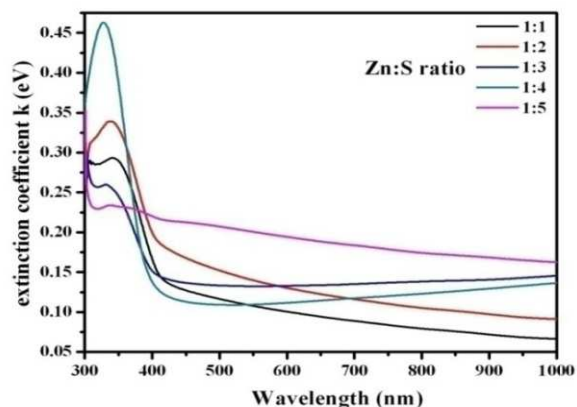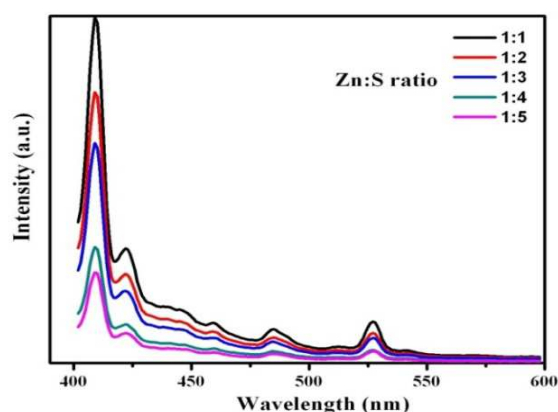
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Fig. (3). The plot of (αhv)² vs. photon energy

Fig. (4). The plot of Extinction coefficient Kf vs wavelength of ZnS film

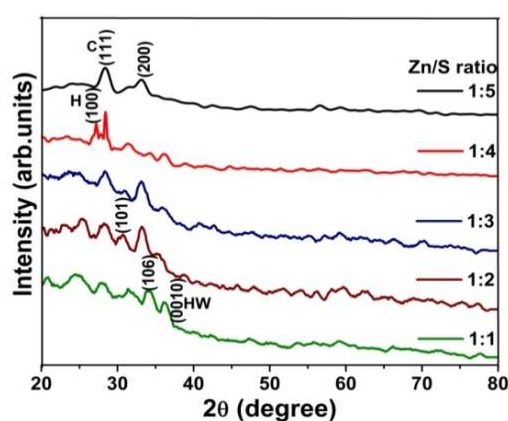**Fig. (5). Photoluminescence spectra of ZnS thin film**

Fig. (6). XRD pattern of ZnS thin film

3.3 Structural studies

The XRD pattern of ZnS thin film is shown as above (Fig 6). It is clearly seen that all the diffraction peaks are well indexed to the standard diffraction pattern of hexagonal and cubic ZnS phases (JCPDS card NO. 89-2344 and JCPDS card NO. 05-0566). A polycrystalline nature is observed for all the deposited films. There is a modification in crystal structure from hexagonal to cubic with increase in sulphur concentration. The crystallite size of the deposited films was decreased from 42 nm to 8 nm by varying the Zn:S ratio. The grain size (D) was calculated from the full width at half maximum (FWHM) (β) by using the Scherer's formula,

$$D = \frac{0.94\lambda}{\beta \cos\theta} \tag{7}$$

Where λ is the wavelength of X-ray (1.5405Å) and θ is the Bragg's angle.

CONCLUSION

The ZnS thin films exhibit an average transmittance of 85% along the range, confirming the suitability of the films to be used as a buffer layer in photovoltaic applications. The band gap varies from 3 to 3.75 eV. The presence of intrinsic and extrinsic defects is confirmed through PL spectra. The XRD patterns show the standard diffraction pattern of hexagonal and cubic ZnS phases. From these studies, we conclude that the results are very much suitable for optoelectronics   and nano electronics devices.

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