Original Research Article

Optical and Electrical Properties of Semiconducting ZnS thin film Prepared by Chemical Bath Deposition Technique

ABSTRACT

The main purpose of this study is to synthesize and investigate the optical and electrical properties of ZnS thin film which has some interesting optoelectronic properties. The films were grown by chemical bath deposition (CBD) technique on clean soda-lime substrates at room temperature (300k). The films were characterized using Fourier transform infrared spectroscopy (FTIR), Ultraviolet-Visible spectroscopy (UV-Vis), and Four point probe measurements. The FTIR spectrum of the film revealed the characteristic ZnS absorption bands below 800 cm^{-1}. The optical properties were studied in the spectra range of 300 to 1500 nm. The film revealed an average transmittance of above 80% in the visible and near infrared regions with a band gap of 3.30 eV. Optical constants of refractive index, extinction coefficient, electrical susceptibility, dielectric loss were estimated at λ = 800 nm. The values of 1.25 Ω.cm and 8.0×10^{-1} $(\Omega.cm)^{-1}$ were obtained as the electrical resistivity and conductivity respectively. The determined properties categorize ZnS thin film as a promising material for various optoelectronic devices.

Keywords: thin films; susceptibility; dielectric; resistivity; spectroscopy.

1. INTRODUCTION

Semiconducting materials like zinc sulphide (ZnS) thin films have attracted the attention of many researchers due to their potential application in different field of science and technology. Zinc sulphide as a group II-VI semiconducting material has properties such as direct electronic transition, large band gap, abundance in nature and never toxic [1,2]. Consequently, it finds application in devices such as light emitting diodes, solar cells, anti-reflective coatings, electro-luminescence displays, multilayers dielectric filters, sensor, lasers, and catalysis [3,4].

In recent years, a great deal of interest has been given to the investigation of the properties (optical and electrical) of ZnS thin films in order to finding new device applications and also improve on the performance on the established ones [5]. The properties of ZnS are function of the deposition parameters and the techniques applied. Therefore, investigating the properties of the film with respect to the different deposition technique is a matter of high importance.

ZnS thin films have been prepared by different techniques which include chemical spray pyrolysis, sputtering, metal organic chemical vapour deposition technique, sol-gel chemical technique, electron beam evaporation, molecular beam epitaxy, electrostatic assisted aerosol jet deposition and chemical bath deposition [6-8]. Among these different ZnS thin film deposition techniques mentioned above, chemical bath deposition technique is one of the most attractive form of thin film deposition methods due to its ease of growing films with non-sophisticated materials and equipment, large area deposition and technically straight forward [9,10]. Since chemical bath deposition is a low temperature deposition processes, better orientation of crystallites with improved grain structure is achieved by controlling the deposition parameters [11]. In view of this, an effort has been made to deposit and characterize ZnS thin films using chemical bath deposition technique (CBD).

2. EXPERIMENTATION

Substrates cleaning are important part of thin films deposition process. Commercially available soda-lime substrates used for the study were soak in Acqua Regia for about 50 minutes and then watched thoroughly with detergent. Finally, the substrates were dried with acetone and stored in a hot oven set at 50^{O}C. ZnS thin films were prepared on clean soda-lime substrates using chemical bath deposition (CBD) at room temperature. The reaction bath consist of zinc acetate and thiourea as the sources of the metal (Zn^{2+}) ion and sulphide (S^{2-}) ion respectively, ammonia solution, distilled water and complexing agents. Triethanolamine (TEA) was used to slow down the reaction and avoid precipitates. Distilled water was carefully added to make a total volume of 50ml. The mixtures were carefully stirred to maintain homogeneity with a constant pH kept at 9.0. The substrates were vertically placed inside the vessel with the help of a locally designed substrate holder. After a time period of 24 hours, the substrates were removed from the bath and washed with distilled water and dried in air.

The resultant films were subjected to characterization studies. The chemical properties were examined using Fourier transform infrared (FTIR) spectroscopy. FTIR spectrum of the powder sample was analyzed using Shimadzu 8400 FTIR Spectrophotometer. The spectrum was obtain using pellets of the prepared powder sample in potassium bromide (KBr) background in the range of wavelength 4000 – 400 cm^{-1}. To study the electronic interaction of the deposited film, UV-Vis measurements were performed using a Janway 6405 UV-Vis Spectrophotometer in the range of 300 to 1500 nm. While the electrical properties were investigated using Old Jandel (TY242MP) four point probe technique. The set-up was made in such a way that the voltages (V) across the film and the corresponding currents (I) were measured using a silver paste to ensure electrical contact.

3 RESULTS AND DISCUSSION

3.1 FTIR Spectroscopic Study

The FTIR characterization was undertaken to determine the formation of ZnS and associated functional groups present on the surface of the sample. Figure 1 shows the FTIR spectrum of ZnS powder in KBr background. An examination of the spectrum showed that the powder exhibits the basic absorption frequency bands between 4000 and 400cm^{-1}. The band observed at 3431cm^{-1} corresponds to the O-H group emanating from water [12]. Other bands include; a very small peak for N-H at 3257$cm^{-1,}$ C-H vibration between 2918 and 2854 cm^{-1}. The regions between 2353 and 1867 cm^{-1} consist of C≡C vibration, C=O vibration is seen at 1138cm^{-1}, C-C stretching vibration at 997 cm^{-1}. Zn-S band was observed below 800cm^{-1}. The peaks matched well with those of ZnS thin film spectrum reported in literature [13, 14].

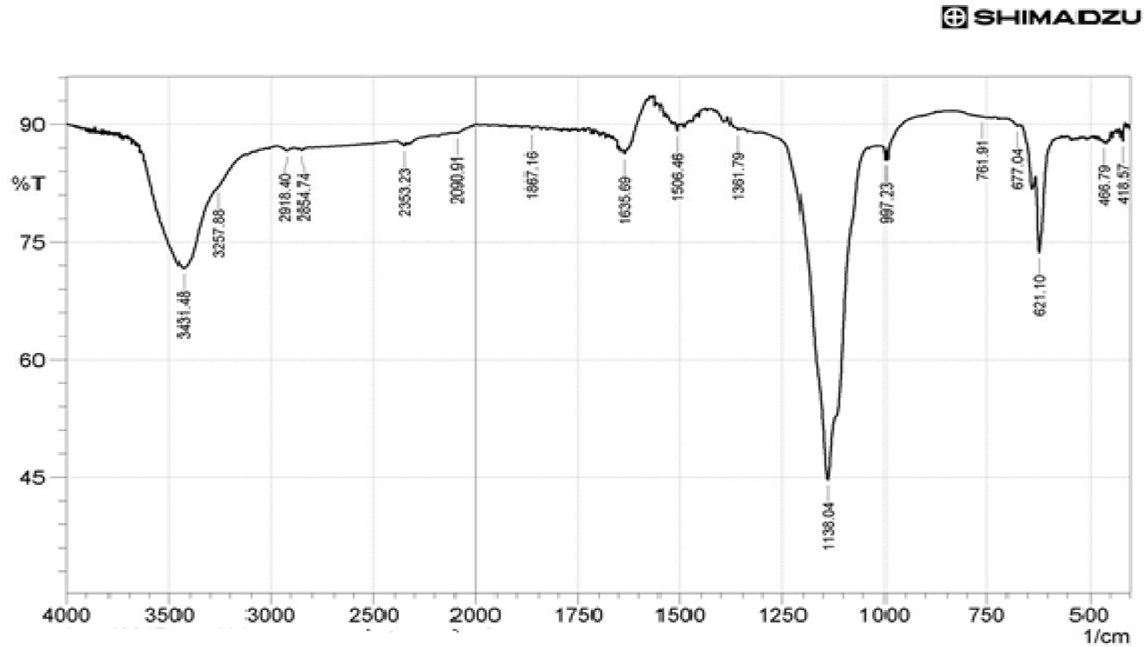

Fig. 1. FTIR spectrum of ZnS powder

3.2 Optical Characterization

The optical measurement constitutes the most direct approach for determining the band structure of ZnS thin films. The Ultraviolet-visible spectrophotometer gave the absorbance of the film as a function of wavelength.. Thus the absorption coefficient (α) is evaluated using the relation [15]

$$\alpha = \frac{1}{W} \ln \frac{1}{T} \qquad (1)$$

where W is the thickness of the film whose value is 308 nm, T is the transmittance and it is estimated using the equation [16]

$$T = 10^{-A} \qquad (2)$$

The transmittance spectrum in Figure 2 shows an increase in transmittance with wavelength, and this is in agreement with the observations made by Ikhioya and Agobi [16] and Ebrahimi *et al.*[17]. Also it has been observed that below 500 nm, there is a sharp fall in the transmittance of the film which is due to the strong absorbance of the film in this region [10]. The film shows low transmittance in the UV region which increased with increasing wavelength towards the Visible and near infrared regions of the electromagnetic spectrum. The relatively lower transmittance in the UV region exhibited by the film suggests that ZnS thin film can be exploited for possible application in screening off harmful UV portion of the electromagnetic spectrum which is detrimental to both animals and humans health [11]. The observed high transmittance in the visible and near infrared regions makes the film a useful material for solar cells and pyro-electric detection [9,16].

The absorption coefficient of ZnS thin film has been observed to obey the exponential relation [18];

$$\alpha = \frac{B}{h\upsilon}[h\upsilon - Eg]^m \quad (3)$$

where *B* is a constant, Eg is the optical band gap energy and the index m can be any value between ½ and 3 depending on the nature of the inter-band electronic transition. It has been established that for ZnS as a direct allowed band gap semiconductor, the exponent in Equation 3 fits well for m = ½ [4], Therefore;

$$\alpha = \frac{B}{h\upsilon}[h\upsilon - Eg]^{½} \quad (4)$$

Figure 3 shows the plot of the square of the absorption coefficient against photon energy which was accomplished using Equation 4. The band gap value of the deposited film was determined by extrapolating the linear portion of the graph to zero. As can be seen from the figure, the band gap energy is equal to 3.30 eV. This result agrees with several studies on semiconducting ZnS thin films obtained in literature [2, 4, 6].

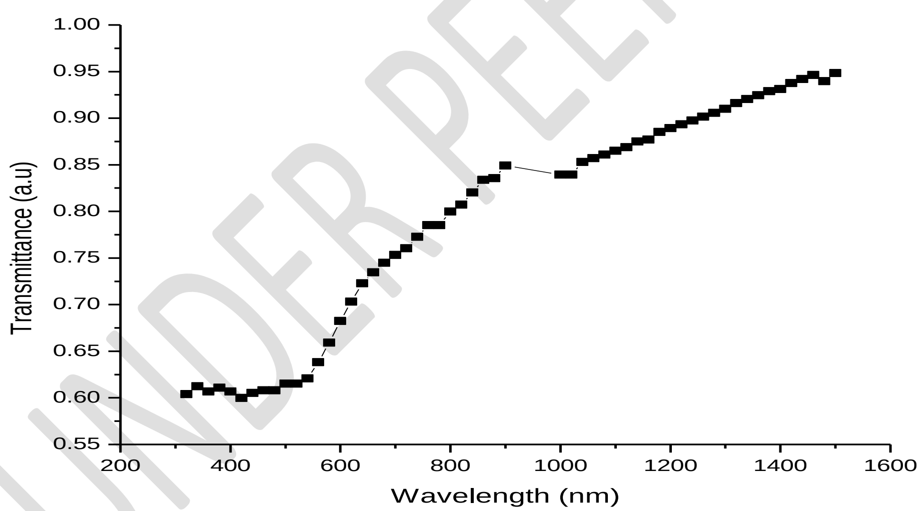

Fig. 2. Transmittance versus wavelength of ZnS thin film

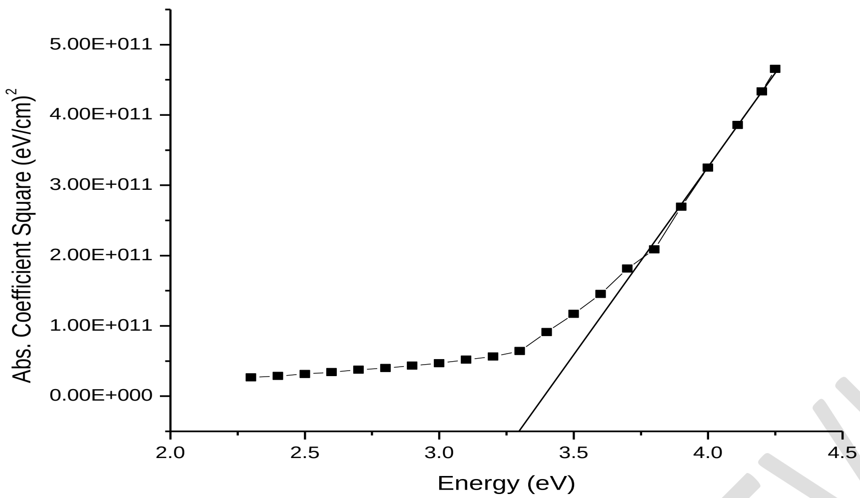

Fig. 3. The plot of square of Abs. coefficient versus energy for ZnS thin film

The refractive index (n) and extinction coefficient (k) are two fundamental properties of an optical material due to the close relationship with the electronic polarization of the ions [19]. So, determining these properties of a semiconducting material is important for potential applications in optoelectronics device like switches, filters and modulators. etc [19,20]. The refractive index (n) of a material could be obtained from the corrected reflectance (R) data using a computational method [21];

$$n = -\frac{(R+1) \pm \sqrt{3R^2+10R-3}}{2(R-1)} \qquad (5)$$

The value of the refractive index (n) was 2.04 at λ =800 nm. The range of the refractive index makes ZnS film suitable for use in optoelectronic devices.

The extinction coefficient (k) of the material could be calculated using the following equation,

$$k = \frac{\alpha\lambda}{(4\pi)} \qquad (6)$$

Here, α is the absorption coefficient of the material. The extinction coefficient (k) was found to be 0.0092 at λ = 800 nm.

From the classical theory of dielectric materials, the electrical susceptibility (X_e) which determines the polarization of a material with respect to applied electric field is estimated using the relation;

$$X_e = \varepsilon - 1 \qquad (7)$$

Where ε is the dielectric constant of the material. Also from Naseem, 2010. [22];

$$n = \sqrt{\varepsilon} \qquad (8)$$

hence, we have

$$X_e = n^2 - 1 \quad (9)$$

when n is the refractive index, the value of the electrical susceptibility is equal to 3.16 at λ= 800 nm. Since the value of X_e is greater than 1, the material can easily be polarized in response to the field therefore, reducing the stored energy within the film [21].

It is well known that the dielectric constant (ε) of a material is directly related to the density of states within the energy gap and depends on the electronic structure of the material. It is fundamentally an intrinsic property of a material that is express as follows;

$$\varepsilon = \varepsilon_r + \varepsilon_i \quad (10)$$

where ε_r and ε_i are the real and imaginary part of the dielectric constant. The real part ε_r is associated with the speed of light in the material while the imaginary part ε_i is concern with the energy absorption due to dipole motion from the field [23]. The real (ε_r) and the imaginary (ε_i) part of the dielectric constant could be estimated using the following expressions

$$\varepsilon_r = n^2 – k^2 \quad (11)$$

$$\varepsilon_i = 2\pi k \quad (12)$$

the values of the real and imaginary dielectric constant at λ = 800 nm were 3.699 and 0.0028 respectively. The values of the dielectric complex are capable of inducing polarization from the electromagnetic light.

The energy loss is related to the optical properties through the dielectric constant. It is concern with the loss of energy associated with the heating of the dielectric material in an electric field [23,24]. The dielectric loss was determine using the relations

$$\tan \Phi = \frac{\varepsilon_i}{\varepsilon_r} \quad (13)$$

and

$$\text{loss angle } \Phi = \tan^{-1}\left(\frac{\varepsilon_i}{\varepsilon_r}\right) \quad (14)$$

Therefore dielectric energy loss and the loss angle at λ = 800 nm were found to be 1.32×10^{-5} and 0.0434 respectively.

3.3 Electrical Properties

The electrical (I-V) analysis of ZnS film was observed using four point probe method. The average current and the corresponding voltage are illustrated in Figure 4. We observed that the current flowing through the film increases linearly with the voltage of the electrode. This implies higher conductivity of the film which may be helpful in obtaining higher frequency in solar cell fabrication [21]. The average current and voltage were found to be 2.213×10^{-7} A and 19.8×10^{-2} V respectively.

The resistivity (ρ) was estimated using the relation [25];

$$\rho = \frac{\pi}{ln2}\left(\frac{V}{I}\right)\times W \qquad (15)$$

Here W is the thickness (308 nm), V and I are the average voltage and current of the film respectively. The reciprocal of the resistivity was taken as the conductivity (σ) of the film.

$$\sigma = \frac{1}{\rho} \qquad (16)$$

from the values of resistivity (ρ) and thickness (W) , the sheet resistance (R_s) can be determined as

$$R_s = \frac{\rho}{W} \qquad (17)$$

The sheet resistance was found to be 4.06×10^6 Ω/Sq., the resistivity was calculated to be 1.25 Ω.cm and the conductivity was also calculated to be 8.0×10^{-1} $(\Omega.cm)^{-1}$. The electrical conductivity value falls within the magnitude of 10^{-13} to 10^2 reported for semiconducting thin films in literature [3], suggesting that the deposited film is conductive in nature. The observed high resistive value of the film indicates that it could find application as semiconducting sensors.

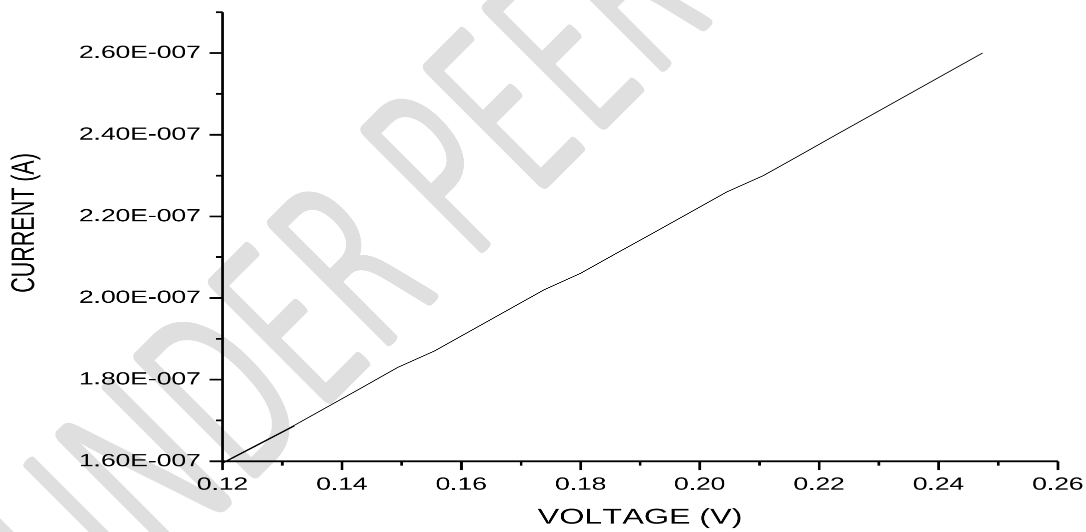

Fig. 4. I-V characteristic of ZnS thin film

4. CONCLUSION

Zinc sulphide (ZnS**)** thin films were prepared by chemical bath deposition technique at room temperature for a period of 24 hours. The deposited films were characterized and the result showed that the film possesses a high transmittance in the visible and near infrared regions with a band gap of 3.30 eV. The spectrum equally revealed other optical properties such as the refractive index, extinction coefficient, electrical susceptibility and dielectric loss which were analyze for device applications. The electrical characterization of the film using four point probe measurement gave the values of resistivity and conductivity to be 1.25 Ω.cm and 8.0 $\times 10^{-1}$ $(\Omega.cm)^{-1}$ respectively. The excellent optical and electrical properties of the deposited film make it useful as window materials in thin film technology and applicable in the manufacturing of thin film embedded resistors.

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