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INVESTIGATION OF THE OPTICAL AND ELECTRICAL PROPERTIES OF TIN SULFIDE THIN FILMS

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Tin sulfide (SnS) thin films were prepared by chemical bath deposition method. The XRD, SEM, UV-Visible absorption spectrum and dielectric studies were used to characterize the synthesized SnS films. The X-ray diffraction (XRD) analysis was used to study the structure and the crystallite size of SnS thin film. The surface morphology was studied using Scanning Electron Microscopy (SEM).The optical properties were studied using the UV-Visible absorption spectrum in the wavelength range of 400 - 900 nm. Optical constants such as band gap, refractive index, extinction coefficient and electric susceptibility were determined from UV-Visible absorption spectrum. The dielectric properties of SnS thin films were studied at different frequencies and temperatures. Further, electronic properties such as valence electron plasma energy, average energy gap or Penn gap, Fermi energy and electronic polarizability of the SnS thin films were calculated. Photoconductivity measurements were carried out to ascertain the positive photoconductivity of the SnS Thin films.

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1. Introduction

The recent examinations in the field of photovoltaics have been directed towards the development of cost effective and non-toxic materials that can be synthesized by an easy technology for solar cell fabrication. In recent years, thin films of SnS have received much consideration for the photovoltaic applications due to their high absorption coefficient and high conductivity [1]. SnS thin film has been used as an absorption layer in the manufacture of heterojunction solar cell due to its narrow band gap [2, 3]. It is one such compound that belongs to IV-VI group with orthorhombic structure. Tin sulfide is a semiconductor, which can be easily prepared by the chemical deposition method [4]. Its thin film is a promising material as an absorber layer for mass production of inexpensive photovoltaic cells, since it has an energy gap of ~ 1.3eV [5]. The film in this study was grown by chemical bath deposition (CBD) which creates a thin film on a solid substrate via a reaction in a liquid solution. The CBD method is inexpensive, easy to prepare and the necessary apparatus can be found in an ordinary chemistry laboratory. Therefore, this method has many advantages over others used to grow semiconductor thin films. This study reports the synthesis and characterization of SnS thin films. The SnS thin films were characterized by X-ray diffraction, scanning electron microscopy (SEM), UV analysis, dielectric studies and Photoconductivity measurement.

2. Experimental procedure

The chemical bath deposition method (CBD) is based on a chemical reaction between dissolved precursors in aqueous solution. The substrate cleaning is very important in the

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deposition of thin films. Commercially available glass slides with a size of 75 mm × 25 mm × 2 mm were washed using soap solution and subsequently kept in hot chromic acid and then cleaned with deionized water followed by rinsing in ethanol. Finally, the substrates were ultrasonically cleaned with deionized water for 10 min and wiped with acetone and stored in a hot oven. Tin chloride (0.2M), sodium thiosulphate, disodium ethylenediaminetetraacetate (0.2M) and hydrochloric acid were used. Aqueous solutions of tin chloride, sodium thiosulfate and disodium ethylenediaminetetraacetate were separately prepared before the experiment. Tin chloride and disodium ethylenediaminetetraacetate were mixed in a beaker. Then, sodium thiosulphate was added into mixture. A glass substrate was placed vertically inside the vessel with the help of a suitably designed substrate holder. After a time period of 30 min, the glass slide was removed from the bath and cleaned with deionized water and dried in the hot oven. The deposited film was taken out from the chemical bath after 30 minutes, rinsed with distilled water, dried in a hot oven at 80°C for 30 minutes and kept in a desiccator. The resultant films were homogeneous and well adhered to the substrate with mirror like surface. The deposited good quality SnS thin films were subjected to characterization studies. The XRD pattern of the SnS thin films was recorded by using a powder X-ray diffractometer (Schimadzu model: XRD 6000 using CuKα (λ=0.154 nm) radiation, with a diffraction angle between 20° and 60°. The crystallite size was determined from the broadenings of corresponding X-ray diffraction peaks by using Scherrer's formula. Scanning Electron Microscopy (SEM) studies were carried out on JEOL, JSM- 67001. The optical absorption spectrum of the SnS thin films was taken by using the VARIAN CARY MODEL 5000 spectrophotometer in the wavelength range of 400 – 900 nm. The dielectric properties of the SnS thin films were analyzed using a HIOKI 3532-50 LCR HITESTER over the frequency range 50Hz-5MHz. Photoconductivity measurements were carried out at room temperature by connecting substrates containing the SnS thin films in series with a picoammeter (Keithley 480) and a dc power supply.

3. Results and discussion

3.1. X-ray diffraction Analysis

The phase composition and the structure of the film were studied by X-ray diffraction analysis. The XRD patterns of the SnS thin films are shown in Fig.1. The XRD patterns reveal diffraction peaks (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of the zinc blend structure of SnS. The XRD results reveal that the deposited SnS thin films with orthorhombic structure having (040) plane. Knowing the wavelength (λ), full width at half maximum (FWHM) of the peaks (β) and the diffracting angle (θ), Particle size (D) was calculated by using the Scherrer formula

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

The average size of the SnS was found to be ~23.6 nm.

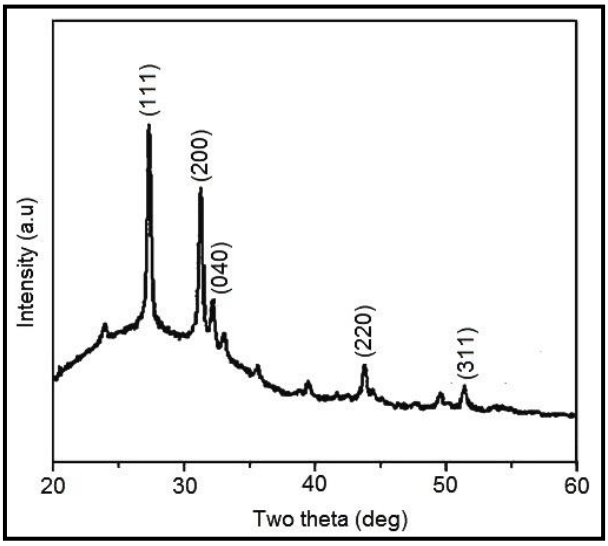

Fig.1.XRD spectrum of SnS thin films

3.2. SEM Analysis

Scanning electron microscope (SEM) was used for studying the surface morphology and micro structural features of the as-prepared SnS thin films. SEM images give information about the surface structure and roughness. It can be seen that the surface of the SnS film is well covered, having unusual distribution of grains. The surface structure of the SnS film deposited on a glass substrate shows some prominent granules of different sizes present on the surface.

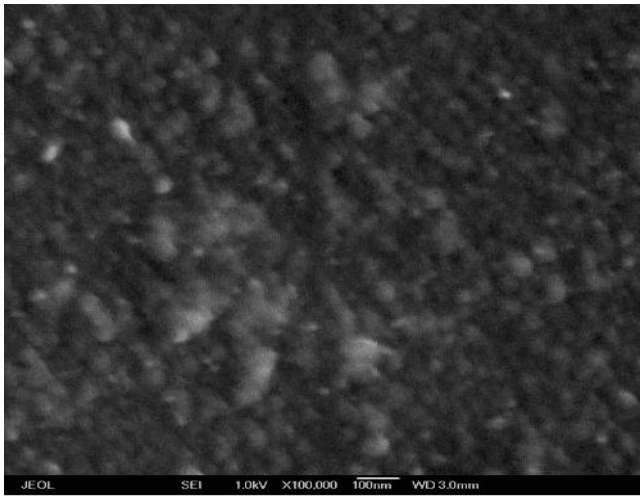

Fig.2. SEM Image of the SnS thin films

3.3. Optical studies

Optical properties are very significant as far as applications in any optoelectronic devices are concerned. In the present study, optical characterization was done for the determination of nature of absorption spectrum and energy bandgap of SnS thin films. The optical absorption spectrum of SnS films was recorded in the wavelength region 400 – 900 nm and it is shown in Fig.3 (a). It is important to note that the SnS films were very much transparent in the visible region. The dependence of optical absorption coefficient on photon energy helps to analyze the band structure and the type of transition of electrons.

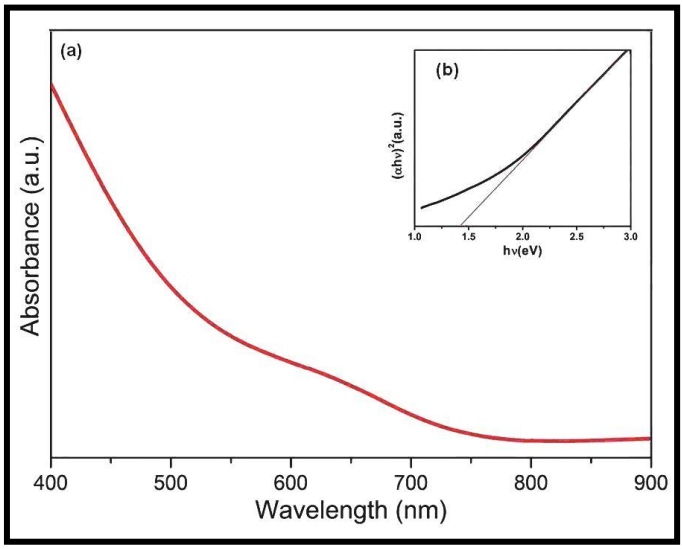

Fig.3 (a) UV-Visible absorption spectrum of SnS films and (b) Plot of $(\alpha h\nu)^2$ Vs photon energy

The optical absorption coefficient (α) was calculated from the transmittance using the following relation

$$\alpha = \frac{1}{d}\log\left(\frac{1}{T}\right) \tag{2}$$

where T is the transmittance and d is the thickness of the film. Determination of optical band gap is based on the photon induced electronic transition between the conduction band and the valance band. The film under study has an absorption coefficient (α) obeying the following relation for high photon energies (hν) and can be expressed as

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu} \tag{3}$$

where E_g is the band gap of the SnS films and A is a constant. A plot of variation of $(\alpha h\nu)^2$ versus hν is shown in Fig.3 (b). Using Tauc's plot, the energy gap (E_g) was calculated to be 1.40 eV.

3.3.1 Determination of Optical Constants

Two of the most important optical properties, namely the refractive index and the extinction coefficient are generally called optical constants. The amount of light that transmitted through thin film material depends on the amount of the reflection and absorption that takes place along the light path. The optical constants such as the refractive index (n), the real dielectric constant (ε_r) and the imaginary part of dielectric constant (ε_i) were calculated.The extinction coefficient (K) can be obtained from the following equation,

$$K = \frac{\lambda\alpha}{4\pi} \tag{4}$$

The extinction coefficient (K) was found to be 1.42 x 10^{-6} at λ =900 nm. The transmittance (T) is given by

$$T = \frac{(1-R)^2\exp(-\alpha t)}{1-R^2\exp(-2\alpha t)} \tag{5}$$

Reflectance (R) in terms of absorption coefficient can be obtained from the above equation. Hence,

$$R = \frac{1 \pm \sqrt{1 - \exp(-\alpha t + \exp(\alpha t)}}{1 + \exp(-\alpha t)} \tag{6}$$

Refractive index (n) can be determined from the reflectance data using the following equation

$$n = -\frac{(R+1) \pm \sqrt{3R^2 + 10R - 3}}{2(R-1)} \tag{7}$$

The refractive index (n) was found to be 1.78 at λ =900 nm. The high refractive index makes SnS film suitable for use in optoelectronic devices. From the optical constants, electric susceptibility (χ_c) can be calculated using to the following relation

$$\varepsilon_r = \varepsilon_0 + 4\pi\chi_C = n^2 - k^2 \tag{8}$$

Hence,

$$\chi_C = \frac{n^2 - k^2 - \varepsilon_0}{4\pi} \tag{9}$$

whereε_0 is the permittivity of free space. The value of electric susceptibility (χ_c) is 2.17 at λ=900 nm. Since electrical susceptibility is greater than 1, the material can be easily polarized when the incident light is more intense.The real part dielectric constant (ε_r) and the imaginary part dielectric constant (ε_i) can be calculated from the following relations

$$\varepsilon_r = n^2 - k^2 \tag{10}$$

$$\varepsilon_i = 2nk \tag{11}$$

The value of real dielectric constant (ε_r) and imaginary dielectric constant (ε_i) at λ=900 nm were estimated at 2.432 and 7.658 x 10^{-5}, respectively. The lower value of dielectric constant and the positive value of the material are capable of causing induced polarization due to intense incident light radiation.

3.4 Dielectric Studies

The dielectric constant was analyzed as a function of the frequency at different temperatures as shown in Fig.4, while the corresponding dielectric loss is shown in Fig.5. The dielectric constant is evaluated using the relation,

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A} \tag{12}$$

where '*C*' is the capacitance, '*d*' is the thickness of the films, 'ε_o' is the permittivity of free space and '*A*' is the area of the films. The curve reveals that the dielectric constant decreases with increase in frequency and then attains almost a constant value in the high frequency region. This also shows that the value of the dielectric constant increases with an increase in the temperature.

Owing to the application of an electric field, the space charges are stimulated and dipole moments are produced and are called space-charge polarization. Besides this, these dipole moments are rotated by the field applied resulting in rotation polarization which also contributes to the high values. Whenever there is an increase in the temperature, more dipoles are produced and the value increases [6, 7]. Fig.5 shows the variation of the dielectric loss with respect to the frequency for various temperatures. These curves show that the dielectric loss is dependent on the frequency of the applied field, comparable to that of the dielectric constant. The dielectric loss decreases with an increase in the frequency at almost all temperatures, but appears to attain saturation in the higher frequency range at all the temperatures [8-10].

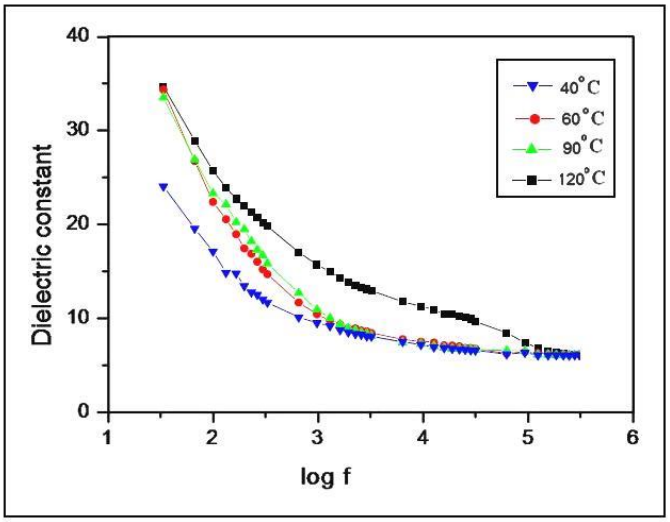

Fig.4. Dielectric constant of SnS thin films

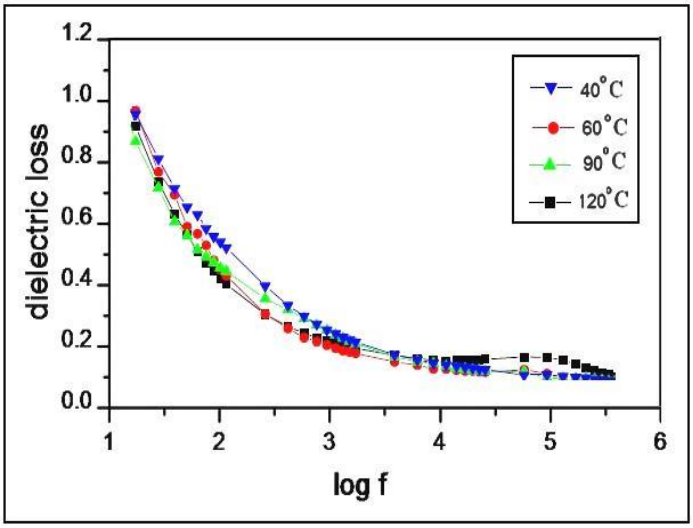

Fig.5. Dielectric loss of SnS thin films

In the proposed relation, only one parameter viz, the high frequency dielectric constant is required as input, to evaluate electronic properties like valence electron plasma energy, average energy gap or Penn gap, Fermi energy and electronic polarizability of the SnS thin films. The theoretical calculations show that the high frequency dielectric constant is explicitly dependent on the valence electron Plasma energy, an average energy gap referred to as the Penn gap and Fermi energy. The Penn gap is determined by fitting the dielectric constant with the Plasmon energy [11]. The following relation [12] is used to calculate the valence electron plasma energy, $\hbar\omega_p$

$$\hbar\omega_P = 28.8\left(\frac{Z\rho}{M}\right)^{1/2} \tag{13}$$

According to the Penn model [13], the average energy gap for the SnS thin films is given by

$$E_P = \frac{\hbar\omega_P}{(\varepsilon_\infty - 1)^{1/2}} \tag{14}$$

where $\hbar\omega_P$ is the valence electron plasmon energy and the Fermi energy [11] given by

$$E_F = 0.2948\,(\hbar\omega_P)^{4/3} \tag{15}$$

Then, the electronic polarizability α, using a relation [14,15],

$$\alpha = \left[\frac{(\hbar\omega_P)^2 S_0}{(\hbar\omega_P)^2 S_0 + 3E_P^2}\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} cm^3 \tag{16}$$

where S_0 is a constant given by

$$S_0 = 1 - \left[\frac{E_P}{4E_F}\right] + \frac{1}{3}\left[\frac{E_P}{4E_F}\right]^2 \tag{17}$$

The Clausius-Mossotti relation also gives

$$\alpha = \frac{3}{4\pi N_a}\frac{M}{\rho}\left[\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}\right] \tag{18}$$

The following empirical relationship is also used to calculate (α) [16],

$$\alpha = \left[1 - \frac{\sqrt{E_g}}{4.06}\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} cm^3 \tag{19}$$

where E_g is the bandgap value determined through the UV absorption spectrum. The high frequency dielectric constant of the materials is a very important parameter for calculating the physical or electronic properties of materials [9, 10]. All the above parameters as estimated are shown in Table 1.

Table.1 Electronic parameters of the SnS thin films

Parameter	**Value**
Plasma energy ($h\omega_p$)	13.13 eV
Penn gap (E_p)	1.72 eV
Fermi Energy (E_F)	11.23 eV
Electronic polarizability (using the Penn analysis)	8.15x 10^{-24} cm^3
Electronic polarizability (using the Clausius-Mossotti relation)	8.23 x 10^{-24} cm^3
Electronic polarizability (using bandgap)	8.10 x 10^{-24} cm^3

3.5 Photoconductivity Studies

Photoconductivity is due to the absorption of photons, creating free charge particles in the conduction band and in the valence band. It gives valuable information about the physical properties of materials and proposes applications in photodetection and radiation measurements. The DC input to the SnS thin films was increased from 0 to 300 volts in steps and the corresponding dark current was noted from the electrometer. For determining the photocurrent, the SnS thin films were illuminated with an incandescent bulb and the corresponding photocurrents were measured. The variation of the photocurrent (I_p) and the dark current (I_d) with applied field are shown in Fig.6.Both the photo and the dark currents of SnS thin films increase linearly with applied voltage. It is observed from the plot that the dark current is less than the photocurrent, suggesting that SnS thin films exhibit positive photoconductivity, which can be attributed to the generation of mobile charge carriers caused by absorption of photons.The positive photoconductivity of the films may be due to the increase in the number of charge carriers to reveal the conducting nature of the material. The dark current was less than the photocurrent, signifying positive photoconductivity nature confirmed by the reported results [17-19].

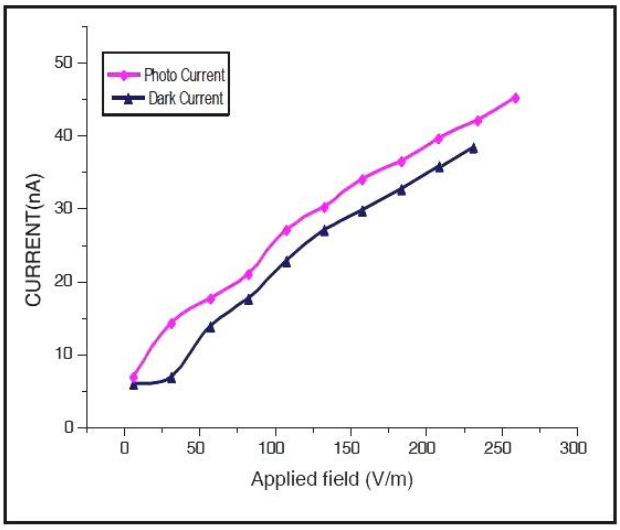

Fig.6Photoconductivity study of SnS Thin films

4. Conclusion

The SnS thin films were prepared by chemical bath deposition (CBD) method. Structural and morphological properties of SnS thin films were investigated by XRD and SEM methods. The XRD studies showed the films are polycrystalline with zinc blend structure. The morphology of the SnS thin films was studied by using SEM studies. The UV-Visible absorption spectrum showed excellent transmission in the entire visible region. The optical constants such as band gap, refractive index, extinction coefficient and electrical susceptibility were calculated to analyze the optical property. The dielectric constant and the dielectric loss of the SnS thin films were calculated at different frequencies and temperatures. In addition, the plasma energy of the valence electron, Penn gap or average energy gap, the Fermi energy and electronic polarizability of the SnS thin films were also determined. The photoconductivity study ascertained the positive photoconductivity nature of the SnS thin films.

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