Doping and annealing effects on structural, optical and electrical characteristics of Sn-doped ZnS thin film

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Abstract
This work presents the fabrication of Zn1−xSnx thin films using the chemical bath deposition method and investigates the effects of Sn doping and annealing temperature on the structural, optical and electrical properties of ZnS thin films. The XRD patterns show that the relative intensities of the major diffraction peaks increase with Sn dopant incorporation and annealing temperature. Because high-temperature annealing forms several nucleation centers throughout the lattice and dopant incorporation enhances point defects leading to crystallite boundary mobility enhancement, crystallinity is also improved. UV–vis–NIR spectrophotometric studies revealed that the films have good transmittance that is larger than 75% in both visible and near-infrared regions and their optical bandgap ranges from 3.34 eV to 3.90 eV. Both the Sn content and annealing temperature cause the transmittance and the optical bandgap to rise. The absorption edge shifts towards the longer wavelength for higher Sn contents and annealing temperatures. Also, the decreased Urbach energy with increased Sn content or annealing temperature can be attributed to the reduced structural disorders and dislocations of ZnS crystals that are indicated by improved crystallinity. Electrical characterization by the two-point probe method exhibits that at higher annealing temperature grain boundary scattering limits the number of mobile carriers by increasing interatomic binding. On the other hand, due to increased carrier concentration and decreased dislocations resulting from the Sn content or annealing, localized carriers dominate in the bulk crystal state and require higher activation energy to replace an interstitial atom and excite the bulk states.

1. Introduction
As a direct and wide bandgap, high refractive index, II–VI semiconductor Zinc Sulphide (ZnS) has shown to have great potentials in optoelectronic applications such as efficient blue or UV light emitters, electroluminescent devices and photovoltaics [1–3]. The material crystallizes in two main forms, namely, cubic zinc blende and hexagonal wurtzite, but the cubic structure is more stable than the hexagonal structure. The cubic form has a direct bandgap of ∼3.6 eV while the hexagonal ZnS has a bandgap of ∼3.91 eV [4, 5].

Material characteristics are severely affected by the amount of dopant and other deposition conditions and in recent years improvement of properties of ZnS by doping metal atoms have been reported particularly for optoelectronic and solar cell applications [6–8]. Doping of ZnS nanocrystals was first reported in [9] where Mn was the dopant. It then followed a series of works on doping ZnS nanoparticles by transition metal ions and rare-earth ions in different preparation methods, for example, ZnS: Mn [10, 11], ZnS: Cu [12, 13], ZnS: Co [14], ZnS: Ag [15], ZnS: Ni [16], ZnS: Sm [17], ZnS: Eu [18] and ZnS: Tb [19]. Structural, optical and electrical properties of lead and bismuth doped ZnS thin films have been studied in [20, 21] while in [22] Mn/Fe-doped and Co-doped ZnS nanowires and nanobelts were synthesized and their magnetic properties were studied for various optical and magnetic devices. To use as polymer light-emitting diodes ZnS based nano-crystalline particles, namely
ZnS: Mn, ZnS: CuCl and ZnS: AgCl were synthesized and characterized in [23]. Resistivity, transmission coefficient and optical bandgap of ZnS thin films have been shown to decrease with the increase of Pb-doping [24]. Besides, Al incorporation has been shown to decrease the crystallite size and increase the dislocation density of electrodeposited ZnS thin films along with lowering the capacitance [25]. Furthermore, heavily Cd-doped ZnS thin films have been shown to increase stacking fault energy and lattice stress and decrease dielectric constant and refractive index [26]. Reference [27] studied chemically deposited tin (Sn-) doped ZnS thin films using polyvinyl pyrrolidone as the surfactant and showed its excellent photocatalytic activity, enhanced radiative decay lifetime and larger surface pore area. Several studies have been performed on the luminescence of Sn doped ZnS [28], for example, the work in [29] used the spray pyrolysis method for the fabrication and reported that 4 at % Sn doping is sufficient to produce blue light-emitting devices. The work in [30] reports that with the increase of Sn doping in chemical bath deposited ZnS thin film optical bandgap and absorption coefficient increase.

Post-synthesis heat treatment plays a significant role in controlling surface defects and high-temperature annealing in an appropriate ambient condition can improve the crystal’s quality, physical properties and ensure stability at a given temperature [31]. Since inappropriate execution of heat treatment can lead to compound decomposition which can degrade the material’s advantageous properties and merits, annealing at the appropriate temperature is crucial to prepare high-quality ZnS films [32]. Therefore, there have been some recent works on the effects of annealing temperature on structural, optical and electrical properties of undoped and doped ZnS films [32–36]. Several growth techniques have been used to deposit thin films, for instance, spin coating [37], molecular beam epitaxy [38], closed space sublimation [39], chemical bath deposition (CBD) [40], pulsed laser deposition [41] and magnetron sputtering [42]. Among these techniques, CBD has many advantages like better parameters controllability, easy tunability, cost efficiency and uniform doping ability. It can develop high-quality films at low temperatures, requires lower evaporation rates and easily coats very large surfaces. Therefore, in this work, we fabricated Zn1₋ₓS:Snₓ thin films using the CBD technique. However, since CBD grown films are either amorphous or poorly crystallized some researchers suggested high-temperature annealing for crystallinity improvement of the films [43].

Further investigation is still required to optimize the properties of ZnS thin films since deposition conditions, temperature and other fabrication parameters heavily influence the material behaviors which might be crucial for various device applications. To our best knowledge, work on the effects of annealing temperatures on structural, optical and electrical properties of Sn-doped ZnS is scarce. Herein, we fabricated Zn1₋ₓS:Snₓ thin films using the CBD method and thoroughly examined the impacts of Sn doping and annealing temperature on the structural, optical and electrical properties of ZnS thin films to determine its potentials for use in different optoelectronic and photonic applications. A systematic study was conducted to investigate the effects of different Sn doping concentrations (12, 16, 20 at %) and different annealing temperatures (150 °C, 200 °C, 250 °C and 300 °C) on the behavior and characteristics of ZnS thin films. We present the outcome of a broad experimental process to find out a variety of physical parameters like crystallite size, micro-strain, defects density, transmission coefficient, Urbach energy, absorption band edge, electron-phonon interaction and steepness parameter as a function of doping and annealing temperature. We precisely calculated current density, Hall coefficient, resistivity, carrier mobility, the energy of activation and carrier concentration.

2. Experimental procedure

Undoped and Sn doped Zinc Sulfide (ZnS) thin films were fabricated on precisely cleaned and well-treated glass substrates. The substrate was kept in chromic acid and further rinsed in acetone and alcohol solutions of equal volume for about 15 min To ensure better adherence, the glass substrate was lightly rubbed and then dipped in bath solution vertically. Chemical bath deposition of Zn1₋ₓS:Snₓ thin film was performed by reacting inorganic reagents Tin Dichloride (SnCl₂) and Zinc Chloride (ZnCl₂) with organic compound Thiourea. To initiate this process, we used 60 ml 0.1 M Zinc Chloride and 120 ml 0.1 M Ammonia in a hot water bath and mixed these two reagents precisely to produce a solution of Hexa-Ammine Zinc Chloride (Zn(NH₃)₂Cl₂). Then 0.5 M Thiourea (SC(NH₂)₂) was added to this solution which further produced Zinc Thiourea Dichloride (Zn(SC)₂(NH₂)Cl₂) solution having pH 9. By following these setups, a layer with a blue shadow was deposited on the previously immersed glass substrate. Thickness was measured by the gravimetric weight difference technique which was found to be 450 nm. To accomplish Sn doping, 0.05 M Tin Dichloride (SnCl₂.2H₂O) was mixed with previously prepared Zinc Thiourea solution and deposition temperature was fixed at 60 °C. In this way, by varying the molar concentration of Zinc Chloride and Tin Dichloride Zn₀.₈₀SₓSn₀.₁₂, Zn₀.₈₄SₓSn₀.¹₆ and Zn₀.₈ₓSₓSn₀.² films were fabricated having thickness 550 nm, 630 nm and 700 nm, respectively. Both of these doped and undoped films were annealed for 60 min at 150 °C, 200 °C, 250 °C and 300 °C.
Using Bragg-Brentano diffraction geometry, phase identification and crystal structure of Zn$_{1-x}$S:Sn$_x$ thin films were analyzed by X’Pert PW-3040 (Philips) diffractometer (at 40 kV, 35 mA). Optical transmission and absorption measurements were performed by a dual-beam UV–vis–NIR spectrophotometer (Shimadzu UV-3600, MPC-3100) and the electrical parameters were measured by using the Hall measurement and dc two-point probe method.

3. Results and discussion

3.1. Structural measurement

Materials characterization using an x-ray diffractometer (XRD) was performed for analyzing crystallographic and structural information of the fabricated ZnS thin films. XRD patterns of Zn$_{1-x}$S:Sn$_x$ ($x =$ 0, 0.12, 0.16, 0.2) thin films annealed at several temperatures ($A_T$) are presented in figure 1 which indicate the origin of cubic zinc selenide structure. An increasing tendency of x-ray diffraction intensity is observed as the amount of Sn dopant and annealing temperature increase because of the gradual increase in the film's thickness (450 nm, 550 nm, 630 nm and 700 nm) and the films with higher thickness have a greater number of crystallites [44, 45]. All the developed Zn$_{1-x}$S:Sn$_x$ films have larger x-ray diffraction intensity at (111) lattice plane compared to (101), (100) and (220) planes. This dominant diffraction intensity at the (111) plane indicates the preferred orientation of crystallinity.

The relative intensities of the major diffraction peaks increase with increasing Sn dopant incorporation. The enhancement of the peak intensity at a higher doping level is a consequence of the formation of new nucleating centers which comes from the reduction of the nucleation energy barrier [46]. The Sn impurity peak for the (311) lattice plane indicates the formation of new nucleating centers and the generation of more stacked electrons throughout the lattice. Besides, heavy Sn doping in ZnS thin film and higher annealing temperature slightly shift the diffraction peaks to larger Bragg’s angles ($2\theta$) because of the localized effect of electronic carriers. The most prominent diffraction peaks corresponding to lattice plane (111) were observed at $2\theta = 35.95^\circ$, 36.01$^\circ$, 36.06$^\circ$ and 36.13$^\circ$ for Zn$_{0.88}$S:Sn$_{0.12}$ annealed at 150 $^\circ$C, 200 $^\circ$C, 250 $^\circ$C and 300 $^\circ$C, respectively. Again for Zn$_{0.8}$S:Sn$_{0.2}$ film, as the annealing temperature increases the major peaks corresponding
to (1 1 1) lattice plane were observed at 2θ = 35.98°, 36.04°, 36.11° and 36.16° for the same annealing temperatures. As the Sn doping content is increased in the ZnS crystal lattice, the substitution of the interstitial atomic position takes place for the variation in the phases which induces slight shifts in the XRD peaks. The shifting of the peaks towards larger Bragg’s angle by Sn doping indicates the compression of the ZnS crystal lattice which is also depicted by the reduction of interplanar spacing. On the other hand, as the annealing temperature increases, both defects of the film and uniform compressive stresses are reduced, and therefore the diffraction peaks are shifted to larger Bragg’s angles [47].

Table 1 shows the interplanar spacing (d-spacing) of Sn doped ZnS thin films at various annealing temperatures (A_t).

| Doping concentration | A_t (°C) | Plane (hkl) | d-spacing (nm) | Doping concentration | A_t (°C) | Plane (hkl) | d-spacing (nm) |
|----------------------|---------|-------------|----------------|----------------------|---------|-------------|----------------|
| Undoped ZnS          | 150     | 100         | 0.5789         | 150                  | 100     | 0.5288      |
|                      |         | 101         | 0.4088         |                      | 101     | 0.1593      |
|                      |         | 220         | 0.2040         |                      | 220     | 0.3733      |
|                      |         | 111         | 0.3327         |                      | 111     | 0.1862      |
| 200 °C               |         | 100         | 0.5756         |                      | 100     | 0.3035      |
|                      |         | 101         | 0.4065         | 200 °C               | 100     | 0.5243      |
|                      |         | 220         | 0.2029         |                      | 311     | 0.1578      |
|                      |         | 111         | 0.3309         |                      | 101     | 0.3696      |
| 250 °C               |         | 100         | 0.5722         |                      | 220     | 0.1844      |
|                      |         | 101         | 0.4041         |                      | 111     | 0.3003      |
|                      |         | 220         | 0.2017         | 250 °C               | 100     | 0.5195      |
|                      |         | 111         | 0.3281         |                      | 311     | 0.1565      |
| 300 °C               |         | 100         | 0.5669         |                      | 101     | 0.3667      |
|                      |         | 101         | 0.4002         |                      | 220     | 0.1831      |
|                      |         | 220         | 0.1997         |                      | 111     | 0.2985      |
|                      |         | 111         | 0.3252         | 300 °C               | 100     | 0.5159      |
| Zn_{0.88}S:Sn_{0.12} | 150     | 100         | 0.5529         |                      | 311     | 0.1554      |
|                      |         | 101         | 0.1664         |                      | 101     | 0.3641      |
|                      |         | 101         | 0.3895         |                      | 220     | 0.1818      |
|                      |         | 220         | 0.1944         |                      | 111     | 0.2964      |
|                      |         | 111         | 0.3166         | Zn_{0.8}S:Sn_{0.2}  | 150     | 0.5125      |
| 200 °C               |         | 100         | 0.5469         |                      | 311     | 0.1543      |
|                      |         | 101         | 0.1646         |                      | 101     | 0.3617      |
|                      |         | 101         | 0.3855         |                      | 220     | 0.1804      |
|                      |         | 220         | 0.1923         |                      | 111     | 0.2937      |
|                      |         | 111         | 0.3133         | 200 °C               | 100     | 0.5075      |
| 250 °C               |         | 100         | 0.5411         |                      | 311     | 0.1528      |
|                      |         | 101         | 0.1629         |                      | 101     | 0.3581      |
|                      |         | 101         | 0.3815         |                      | 220     | 0.1787      |
|                      |         | 220         | 0.1903         |                      | 111     | 0.2914      |
|                      |         | 111         | 0.3100         | 250 °C               | 100     | 0.5038      |
| 300 °C               |         | 100         | 0.5355         |                      | 311     | 0.1518      |
|                      |         | 101         | 0.1612         |                      | 101     | 0.3557      |
|                      |         | 101         | 0.3775         |                      | 220     | 0.1776      |
|                      |         | 220         | 0.1884         |                      | 111     | 0.2897      |
|                      |         | 111         | 0.3067         | 300 °C               | 100     | 0.5015      |

Table 1. Interplanar spacing (d-spacing) of Sn doped ZnS thin films at various annealing temperatures (A_t).

The improvement of crystallinity by the increase of annealing temperature happens because of the relieving of the stress which includes thermal stress and intrinsic stress. One of the main reasons for the appearance of

\[ a = \frac{1}{h^2 + k^2 + l^2} \]
intrinsic stress by the substrate is the coalescence of the adjacent grain boundaries which generates the tensile stress \[49\]. During the fabrication process, variation of lattice parameters of the film and the substrate produces mismatch stress because of the interfacial misalignment as reported in \[50\]. Moreover, owing to the lattice compression, discrepancies occur at the substrate and film interface that resist the film’s lattice compression and lead to the tensile stress \[51\]. On the other hand, the discrepancies of the thermal expansion coefficients of the film and the substrate cause thermal stress while the variation in unstrained crystal spacing of the film and the substrate gives rise to intrinsic stress (\(\psi\)) into the lattice structure. The intrinsic stress developed in the fabricated films can be obtained by comparing the measured lattice constant (\(a\)) with its bulk state value and is calculated by using the following equation \[24\].

\[
\psi = \frac{Y (a - a_0)}{2a\gamma}
\]

Here \(Y\) represents Young’s modulus which is 75 GPa for ZnS, \(a_0\) is the bulk lattice constant (0.5407 nm) and \(\gamma\) is the Poisson’s ratio (0.27 for ZnS). Variations of intrinsic stress of ZnS thin film as a function of Sn content and annealing temperature is shown in figure 3 which demonstrates the reduction of intrinsic stress with the increase of both Sn doping and annealing temperature. To quantify, undoped ZnS thin film annealed at 150 °C has intrinsic stress of 9.188 GPa for (100) plane which is reduced to 7.66 GPa for the same plane annealed at 250 °C. Again, Zn0.88S:Sn0.12 film for (100) plane has intrinsic stress of 3.08 GPa for 150 °C annealing and this value is decreased to 1.59 GPa for 200 °C annealing. The reduction of intrinsic stress is due to the reduced interatomic separation and minimized delocalized carriers that compress the separation of unstrained spacing of ZnS lattice and the glass substrate.

The average crystallite sizes (\(S_C\)) of Zn\(_{1-x}\)S:Sn\(_x\) thin films are estimated using the Debye–Scherrer formula in equation (3) \[52\] for varying annealing temperatures and shown in figure 4.

\[
S_C = \frac{K \times \lambda}{\beta \times \cos \theta}
\]

Here, \(K\) is dimensionless shape factor (0.94), \(\lambda\) is x-ray photon wavelength (0.154 nm), \(\beta\) is full-width at half maximum (FWHM) in radians and \(\theta\) is Bragg diffraction angle. FWHM and the diffraction angle (\(\theta\)) for Zn\(_{1-x}\)S:Sn\(_x\) films with different annealing temperatures are shown in table 2. It is seen that with the rise of the annealing temperature, the FWHM values go down whereas the crystallite size increases suggesting improvement of crystallization by the increase of annealing temperature. After the deposition process, high...
temperature annealing forms several nucleation centers throughout the lattice and the incorporation of more Sn dopants enhances the concentration of point defects which could lead to crystallite boundary mobility enhancement and ultimately producing bigger size crystallites. Therefore, as shown in figure 4, heavily Sn doped...
ZnS thin films at high annealing temperature have larger crystallite sizes compared to lightly doped films with lower annealing temperatures. For instance, the crystallite size of undoped ZnS thin film annealed at 150 °C increases from 27.36 nm to 30.68 nm at 250 °C annealing. Furthermore, the crystallite size of Zn$_{0.84}$S:Sn$_{0.16}$ thin film annealed at 150 °C goes up from 45.67 nm to 48.75 nm for 300 °C annealing temperature.

Geometric defects originated at the Brillouin zone and the increased compressive stress produces a new parameter micro-strain ($M_S$). In other words, micro-strain is caused by a geometric mismatch at inter-phase boundaries between the crystalline lattice of films and substrates. It is estimated by the following equation [52]:

$$M_S = \frac{\beta \times \cos \theta}{4}$$  \hspace{1cm} (4)

Micro-strain influences film strength, cracking and hardness and also measures the critical limit of elasticity. Figure 5 shows that the values of micro-strain are decreased with the increase of annealing temperature and incorporated Sn content. This implies that heavily Sn-doped ZnS films have relatively lower lattice mismatches.

### Table 2. Bragg’s angle and full width at half maximum (FWHM) of the deposited Sn doped ZnS films.

| Doping concentration | Annealing temperature ($\Delta T$) | Bragg’s angle (θ) | FWHM (β) |
|----------------------|-----------------------------------|------------------|---------|
| Undoped ZnS          | 150 °C                            | 17.58°            | 0.00555 rad |
|                      | 200 °C                            | 17.63°            | 0.00523 rad |
|                      | 250 °C                            | 17.78°            | 0.00495 rad |
|                      | 300 °C                            | 18.03°            | 0.00475 rad |
| Zn$_{0.88}$S:Sn$_{0.12}$ | 150 °C                            | 18.14°            | 0.00408 rad |
|                      | 200 °C                            | 18.15°            | 0.00394 rad |
|                      | 250 °C                            | 18.17°            | 0.00379 rad |
|                      | 300 °C                            | 18.18°            | 0.00368 rad |
| Zn$_{0.84}$S:Sn$_{0.16}$ | 150 °C                            | 18.20°            | 0.00333 rad |
|                      | 200 °C                            | 18.21°            | 0.00327 rad |
|                      | 250 °C                            | 18.21°            | 0.00320 rad |
|                      | 300 °C                            | 18.19°            | 0.00313 rad |
| Zn$_{0.8}$S:Sn$_{0.2}$  | 150 °C                            | 18.25°            | 0.00289 rad |
|                      | 200 °C                            | 18.26°            | 0.00282 rad |
|                      | 250 °C                            | 18.28°            | 0.00276 rad |
|                      | 300 °C                            | 18.31°            | 0.00269 rad |

Figure 5. Micro-strain of ZnS thin films as a function of Sn doping concentration at varying annealing temperatures ($\Delta T$).
This fact is also reflected in the fluctuations of the diffraction patterns which improve both the crystal misalignment and internal lattice deformation. Films with better crystalline quality and larger crystallite size are produced when there is a lower value of micro-strain. Again, at high annealing temperature because of the increased crystallite size, the interplanar spacing becomes smaller indicating an increase in the interatomic bonding. Such strengthened bonding impedes the lattice from micro-structural deformation and reduces the values of micro-strain. The dislocation density \( \rho \) measures the number of defects in the crystal structure and is estimated using the Williamson and Smallman formula:

\[
\rho = \frac{15 \times M_s}{a \times S_i}
\]  

In figure 6 it is seen that the dislocation density is reduced as either the annealing temperature or the Sn incorporation increases for all the lattice planes. Undoped ZnS thin film annealed at 150 °C has a dislocation density of \( 1.457 \times 10^{11} \) lines cm\(^{-2} \) for (111) lattice plane which is reduced to \( 1.225 \times 10^{11} \) lines cm\(^{-2} \) for 250 °C annealing for the same lattice plane.

Besides, Zn\(_{0.88}\)S:Sn\(_{0.12}\) thin films annealed at 150 °C shows defects density of \( 0.989 \times 10^{11} \) lines cm\(^{-2} \) and it is decreased to \( 0.557 \times 10^{11} \) lines cm\(^{-2} \) when annealed at 300 °C. As seen in equation (5), dislocation density is proportional to micro-strain but inversely proportional to crystallite size. Therefore, the explanation of an increase in crystallite size with the increase of Sn-doping makes it clear why heavily Sn-doped ZnS films have lower dislocation density. Due to the gradual decrease of micro-strain and intrinsic stress with the increase of annealing temperature, disproportionate lattice mechanical strength originates from grain boundary absorption. This reduced lattice hardness lowers the value of dislocation density.

### 3.2. Optical measurement

The deposition method, deposition criteria, annealing conditions and dopant materials severely influence several optical parameters. UV–vis–NIR spectrophotometer is utilized to characterize the optical properties of Zn\(_{1-x}\)S:Sn\(_x\) thin films at several annealing temperatures. The transmission coefficient of Zn\(_{1-x}\)S:Sn\(_x\) thin films as a function of both Sn content and annealing temperature is presented in figure 7 which indicates a relatively larger
transmittance of more than 75% in both visible and near-infrared region. Transmission spectra of undoped ZnS are strongly impacted by the Sn incorporation and annealing temperature. For example, at an incoming wavelength of 1000 nm, undoped ZnS film annealed at 150 °C has 77.32% transmittance which enhances to 79.43% for 300 °C annealing temperature. On the other hand, Zn_{0.84}S_{0.16} films with 150 °C and 300 °C annealing temperatures have the transmittance of 80.07% and 81.33%, respectively. In all cases, increasing Sn content and higher annealing temperature enhance the value of transmittance. The increase of transmittance with the annealing temperature is related to the improvement of crystallization quality which leads to the decline of optical scattering. On the other hand, the enhanced diffraction intensities at higher Sn concentration imply more closely stacked carriers with small interatomic spacing generated in the lattice. These localized carriers are bounded by the electrostatic force of attraction and turn the lattice porous which is further ignited by high annealing treatment. The increased lattice porosity lets more incoming photons transmit through the lattice structure at varying annealing temperatures ($A_T$).

The origin of the material’s electronic states is confirmed by the higher energy part of absorption spectra while different vibrational modes are related to the lower energy part. Using the Beer–Lambert relation in equation (6), the optical absorption coefficient ($\alpha$) is calculated [55]:

$$\alpha = \frac{1}{t} \ln \left[ \frac{(1 - R)^2 + \{(1 - R)^2 + 4R^2T^2\}^{1/2}}{2T} \right]$$

where $t$, $T$ and $R$ stand for film thickness, transmittance and reflectance, respectively. The dependence of the absorption coefficient on Sn doping content and annealing temperature is shown in figure 5 where the absorption coefficient is presented as a function of wavelength. It is seen that all the films have a relatively high absorption coefficient which decreases with the increase in doping contents and annealing temperature. Figure 8 also shows the absorption edge wavelength which is calculated by the extrapolation of the steep portion of the absorption spectra. The influence of annealing temperature and Sn incorporation on the onset of absorption edge wavelength is recorded in table 3. The absorption edge shifts toward longer wavelengths for higher Sn contents and annealing temperatures. But the influence of Sn doping content is more prominent since the absorption edge wavelength of films having higher Sn content at low annealing temperature is higher than the films with lower Sn content even at the high annealing temperature. For example, the absorption edge of

![Figure 7. Transmission spectra of (a) undoped ZnS, (b) Zn_{0.88}S_{0.12}, (c) Zn_{0.84}S_{0.16}, (d) Zn_{0.8}S_{0.2} thin films.](image-url)
Zn$_{0.84}$S:Sn$_{0.16}$ is 1298 nm at 300 °C annealing temperature while that of Zn$_{0.8}$S:Sn$_{0.2}$ is 1480 nm at 150 °C annealing temperature. The optical absorption edge refers to the absorption discontinuity occurring at a certain wavelength and it has a direct correspondence with the energy of an electronic transition [56]. To point out the light–matter interactions of compound semiconductors it is obvious to measure the dipole coupling and the dipole vibrational mode using the absorption edge concept.

From the surface of the film toward its inside, the photon current density reduces exponentially and the depth at which it becomes 1/e of the value at the surface is called the depth of EM wave penetration (δ). The penetration depth depends on the density of the film, refractive index, surface morphology, conductivity and microstructure of the film and is estimated by the following expression:

\[
\delta = \frac{1}{\alpha}
\]  

Depth of penetration for ZnS thin film as a function of doping concentration and annealing temperature is presented in figure 9 which shows a positive correlation of penetration depth with both the annealing temperature and Sn content. For instance, undoped ZnS annealed at 150 °C has a maximum penetration depth of 183.4 nm which enhances to 185 nm for 300 °C, while Zn$_{0.88}$S:Sn$_{0.12}$ has a maximum penetration depth of 185.8 nm and 187 nm for 150 °C and 300 °C annealing temperatures, respectively. It is observed that the film thickness has a positive impact on the enhancement of penetration depth, for example, the penetration depth of Zn$_{0.88}$S:Sn$_{0.12}$ film with 550 nm thickness is higher than that of undoped ZnS having the thickness of 450 nm. The enhancement of penetration depth at heavily Sn-doping and higher temperature annealing is due to the greater number of carriers stacked in the lattice which shortens the chance of interaction of free carriers with incoming EM waves or photons.

Influence of Sn content and annealing condition on optical bandgap ($E_g$) of ZnS thin films is investigated for direct inter-band transition utilizing the values of absorption coefficient and photon energy ($h\nu$) [57]:

![Figure 8. Absorption edge wavelength of (a) undoped ZnS, (b) Zn$_{0.88}$S:Sn$_{0.12}$, (c) Zn$_{0.84}$S:Sn$_{0.16}$, (d) Zn$_{0.8}$S:Sn$_{0.2}$ at different annealing temperatures ($A_t$).](image-url)
Here B is an energy-independent constant. As shown in figure 10, optical bandgap was calculated by extrapolating the linear portion of \((\alpha h\nu)^2\) versus photon energy \((h\nu)\) plot to zero absorption \((\alpha = 0)\). Both Sn content and annealing in ZnS thin film cause the optical bandgap to rise. For instance, undoped ZnS annealed at 150 °C has a bandgap of 3.34 eV which becomes 3.45 eV for 300 °C and for Zn_{0.84}S:Sn_{0.16} at 150 °C annealing bandgap is 3.68 eV which increases to 3.77 eV for 300 °C annealing temperature. The bandgap for all the cases is presented in table 3. The reason for bandgap widening by higher Sn content is attributed to the reduction of lattice parameters and interatomic distances that increase the interatomic bonding. Again, high temperature annealing intensifies the strength of interatomic bonding and enlarges the gap between upper level of valence band and lower level of conduction band.

During the inclusion of the dopants in the thin film semiconductors, some structural disorders and defects are formed that create band tail energies, also known as Urbach tails. Urbach’s absorption edge is established underneath the forbidden energy gap within the region of photon energies. Spectral absorption in materials is controlled by the localized states present around the forbidden bandgap. In other words, the interaction between crystal lattice vibrations and localized states in the Urbach tail region has a noteworthy impact on the optical properties of the thin films [58]. The width of the absorption edge energy of the localized states in the bandgap depends on the degree of structural disorders and is termed as Urbach energy \((E_U)\) [59, 60]. By Urbach’s empiric formula the relationship of absorption coefficient \((\alpha)\) to the incident photon energy \((h\nu)\) can be obtained within the low photon energy range in the Urbach tail region as [61]:

\[
\alpha = \alpha_0 e^{h\nu / E_U}
\]

Here \(\alpha_0\) denotes Urbach constant and \(E_U\) presents Urbach energy or band tail energy. Taking the logarithm of either side of equation (9) we get the equation of a straight line:

\[
(\alpha h\nu)^2 = B \times (h\nu - E_U)
\]

(8)

Figure 9. Depth of penetration of (a) undoped ZnS, (b) Zn_{0.88}S:Sn_{0.12}, (c) Zn_{0.84}S:Sn_{0.16}, (d) Zn_{0.8}S:Sn_{0.2} at different annealing temperatures \((A_t)\).
Urbach energy can be obtained by the reciprocal of change of \( \ln(\alpha) \) per unit change of photon energy as sketched in figure 11 and formulated in equation (11):

\[
\ln \alpha = \ln \alpha_0 + \frac{h\theta}{E_U}
\]  

(10)

Table 3. Values of absorption edge wavelength, Urbach energy, steepness parameter and strength of electron-phonon interaction of the Sn-doped ZnS thin films at varying annealing temperatures \( (A_1) \).

| Doping concentration | \( A_T \) (°C) | Absorption edge wavelength (nm) | Optical bandgap (eV) | Urbach energy, \( E_U (eV) \) | Steepness parameter, \( \sigma \) | Strength of electron-phonon interaction, \( E_{e-p} \) |
|----------------------|---------------|--------------------------------|----------------------|-------------------------------|--------------------------|---------------------|
| Undoped ZnS          | 150           | 817                            | 3.34                 | 0.7685                        | 0.0475                   | 14.035               |
|                      | 200           | 850                            | 3.37                 | 0.7267                        | 0.0561                   | 11.883               |
|                      | 250           | 894                            | 3.42                 | 0.6932                        | 0.0650                   | 10.256               |
|                      | 300           | 927                            | 3.45                 | 0.6658                        | 0.0742                   | 8.984                |
| Zn_{0.88}S:Sn_{0.12} | 150           | 990                            | 3.54                 | 0.5574                        | 0.0654                   | 10.193               |
|                      | 200           | 1026                           | 3.56                 | 0.5239                        | 0.0778                   | 8.568                |
|                      | 250           | 1081                           | 3.59                 | 0.5021                        | 0.0898                   | 7.423                |
|                      | 300           | 1115                           | 3.62                 | 0.4833                        | 0.1022                   | 6.523                |
| Zn_{0.84}S:Sn_{0.16} | 150           | 1150                           | 3.68                 | 0.4165                        | 0.0876                   | 7.610                |
|                      | 200           | 1183                           | 3.70                 | 0.3957                        | 0.1031                   | 6.466                |
|                      | 250           | 1231                           | 3.73                 | 0.3726                        | 0.1210                   | 5.509                |
|                      | 300           | 1298                           | 3.77                 | 0.3564                        | 0.1387                   | 4.806                |
| Zn_{0.8}S:Sn_{0.2}   | 150           | 1480                           | 3.81                 | 0.2786                        | 0.1651                   | 4.037                |
|                      | 200           | 1527                           | 3.84                 | 0.2471                        | 0.2093                   | 3.185                |
|                      | 250           | 1580                           | 3.87                 | 0.2155                        | 0.2578                   | 2.585                |
|                      | 300           | 1654                           | 3.90                 | 0.1917                        |                          |                     |

Figure 10. Optical bandgap of (a) undoped ZnS, (b) Zn_{0.88}S:Sn_{0.12}, (c) Zn_{0.84}S:Sn_{0.16}, (d) Zn_{0.8}S:Sn_{0.2} at varying annealing temperatures \( (A_1) \).
The calculated Urbach energies of Sn-doped ZnS thin films at several annealing temperatures are shown in table 3. Urbach energy of ZnS thin film decreases when the amount of Sn content or the annealing temperature increases. For example, undoped ZnS thin film annealed at 150 °C has Urbach energy of 0.7685 eV which becomes 0.6658 eV for 300 °C annealing and Zn0.84S:Sn0.16 film at 150 °C has Urbach energy value of 0.4165 eV that decreases to 0.3564 eV for 300 °C. Urbach tail implies the level of disorder in the lattice structure which can measure structural integrity. Higher annealing temperature and higher Sn concentration improve crystallinity, reduce the structural disorders and dislocations of ZnS crystals. Because of this Urbach’s tail gets lowered and the optical bandgap gets widened.

Electron-phonon interaction expands the absorption edges and is defined by the steepness parameter (σ) which is estimated by the slope of the straight-line in the absorption curve and is related to the Urbach energy by the following expression:

$$ E_U = \left( \frac{d\ln \alpha}{d(h\nu)} \right)^{-1} $$ (11)

The strength of electron-phonon interaction is directly proportional to the Urbach energy which refers to the structural disorders, lattice imperfections and surface passivation [63]. Estimated values of $E_{e-p}$ at different annealing temperatures and percentages of Sn concentration are recorded in table 3. Higher amount of Sn content and higher annealing temperature enhance the steepness parameter but shrink the magnitude of strength of electron-phonon interaction. For instance, undoped ZnS thin film annealed at 150 °C has $E_{e-p}$ of...
14.035 which is reduced to 10.193 for Zn$_{0.88}$S:Sn$_{0.12}$ and to 7.610 for Zn$_{0.84}$S:Sn$_{0.16}$. Sn doping in ZnS enhances the crystallinity and reduces the structural disorders and therefore compared to undoped ZnS the values of Urbach energy have a sharp transition from 0.7685 eV to 0.5574 eV for 12 at.% Sn: ZnS thin film. In the same way, enhancement in the crystallographic orientation has impacts on the strength of electron-phonon interaction.

Measurement of refractive index ($n$) is performed using reflectance ($R$) and extinction coefficient ($k$) by the following equation:

$$n = \frac{1 + R}{1 - R} + \sqrt{\frac{4R + (1 - R)^2k^2}{(1 - R)^2}}$$  \hfill (14)

Here the extinction coefficient is estimated by the following expression [52]:

$$k = \frac{\alpha \lambda}{4\pi}$$  \hfill (15)

Annealing and Sn doping in ZnS thin film influence its refractive index profile as demonstrated in table 4. It is seen that as the amount of Sn content and annealing temperature increases, the refractive index reduces. For example, undoped ZnS thin film annealed at 150 °C has a refractive index of 1.732 and at 300 °C it becomes 1.665 while Zn$_{0.88}$S:Sn$_{0.12}$ film annealed at 150 °C has a refractive index of 1.613 and at 300 °C annealing it reduces to 1.482. The reduction in the refractive index comes from the reduction in lattice parameter and dislocation density with the increase of Sn concentration. Also, higher annealing treatment eliminates the formation of thermally labile phases as well as decreases the oxidation bonding which produces several pores in the lattice structure [64] and these newly generated pores lower the value of refractive index. The dielectric constant of ZnS thin film is calculated for different annealing and Sn contents using $\varepsilon_r = \frac{1}{\varepsilon_0} = \frac{n^2}{k}$ [64] and is shown in table 4. Here ($n^2 - k^2$) and 2nk are real and imaginary parts of the dielectric constant, respectively. Higher Sn contents and high temperature annealing increase the desorption process of thermally unstable phase groups and these unstable groups reduce the film density that further minimize the value of dielectric constant [65]. Besides, with higher Sn content and annealing, incoming photons have less chance to be reflected. Therefore, the refractive index profile gets reduced and the value of the dielectric constant is decreased.

| Doping concentration | Annealing temperature | Refractive index | Dielectric constant |
|----------------------|-----------------------|------------------|--------------------|
| Undoped ZnS          | 150 °C                | 1.732            | 9.33               |
|                      | 200 °C                | 1.714            | 9.29               |
|                      | 250 °C                | 1.686            | 9.26               |
|                      | 300 °C                | 1.665            | 9.24               |
| Zn$_{0.88}$S:Sn$_{0.12}$ | 150 °C            | 1.613            | 9.17               |
|                      | 200 °C                | 1.607            | 9.14               |
|                      | 250 °C                | 1.588            | 9.12               |
|                      | 300 °C                | 1.572            | 9.09               |
| Zn$_{0.84}$S:Sn$_{0.16}$ | 150 °C            | 1.524            | 9.02               |
|                      | 200 °C                | 1.508            | 8.98               |
|                      | 250 °C                | 1.495            | 8.95               |
|                      | 300 °C                | 1.482            | 8.91               |
| Zn$_{0.8}$S:Sn$_{0.2}$   | 150 °C            | 1.427            | 8.83               |
|                      | 200 °C                | 1.416            | 8.80               |
|                      | 250 °C                | 1.407            | 8.75               |
|                      | 300 °C                | 1.389            | 8.69               |

3.3. Electrical measurement

Studies using Hall measurement and dc two-point probe method attest that annealing conditions as well as Sn doping have a severe impact on the electrical characteristics of ZnS thin films. A graphical representation of the current density curves (J-V) is shown in figure 12 as a function of both Sn content and annealing temperature. The J-V curves show that higher Sn doping and annealing of ZnS thin films reduce the value of current density. For instance, when the applied voltage is 1.5 V, undoped ZnS annealed at 150 °C shows current density of 5.2803 mA cm$^{-2}$ at 150 °C, 4.243 mA cm$^{-2}$ at 200 °C, 3.981 mA cm$^{-2}$ at 250 °C and 3.805 mA cm$^{-2}$ at 300 °C annealing temperatures. For Zn$_{0.88}$S:Sn$_{0.12}$ films, these values undergo a sharp decrease to 3.324 mA cm$^{-2}$ at 150 °C, 3.185 mA cm$^{-2}$ at 200 °C, 2.956 mA cm$^{-2}$ at 250 °C and 2.867 mA cm$^{-2}$ at 300 °C annealing. It is
evident from the structural characterization that high level of Sn contents and high annealing temperature strengthen the planar bonding as a result of sharp reduction in the interplanar spacing. The strong bonding enlarges the gap between the top of the valence band and the lowest level of the conduction band implying a wider optical bandgap. The wider bandgap shrinks the conduction paths of the free carriers and thus reduces the current conduction ability of ZnS thin films.

Carrier mobility, Hall coefficient, resistivity, the energy of activation and carrier concentration for different doping concentrations and annealing temperatures are estimated using Hall measurements in van der Pauw configuration. The findings of the electrical characterization are summarized in table 5. A decrease in carrier mobility with the increase of annealing and Sn doping is observed. For instance, undoped ZnS annealed at 150 °C shows carrier mobility of 192.45 cm² VS⁻¹ which goes down to 181.78 cm² VS⁻¹ for 300 °C annealing while Zn₀.₈S:Sn₀.₂ film at 150 °C annealing has a mobility of 153.69 cm² VS⁻¹ which increases to 152.63 cm² VS⁻¹ for 300 °C annealing. The decrease in the mobility from undoped to doped ZnS might be due to the sudden increase of the crystallites that further increases the grain and particle sizes. The expansion in the grain size induces the grain boundary scattering and increases local ionized impurities which bring down the number of mobile carriers due to the strong bonding and thus reduce the carrier mobility throughout the lattice. The average Hall coefficient increases from 1.47 × 10⁶ cm³/C for undoped ZnS (annealed at 150 °C) to 3.94 × 10⁶ cm³/C for Zn₀.₈S:Sn₀.₂ thin film (annealed at 300 °C) while the carrier concentration also goes up from 4.25 × 10¹⁹ cm⁻³ for undoped ZnS (annealed at 150 °C) to 21.16 × 10¹⁹ cm⁻³ for Zn₀.₈S:Sn₀.₂ thin film (annealed at 300 °C). It is observed that the resistivity increases with annealing temperature but with the incorporation of Sn content the increase is very sharp. The resistivity of undoped ZnS film annealed at 150 °C increases from 13.52 × 10⁴ Ωcm to 48.06 × 10⁴ Ωcm for Zn₀.₈S:Sn₀.₂ film annealed at 300 °C. With the enhancement of Sn doping content and annealing temperature, the numbers of crystallites and localized carriers increase which continuously collide with each other. The increased interaction among the localized states results in the surface and grain boundary scattering which ultimately makes the electrical resistivity larger and increases the corresponding electrical power dissipation. At lower doping concentration dopant Sn substitution in the grain boundaries leaves additional electrons that act as donors. On the other hand at higher doping

Figure 12. Current density (J-V) curves of (a) undoped ZnS, (b) Zn₀.₈₈S:Sn₀.₁₂, (c) Zn₀.₈₄S:Sn₀.₁₆, (d) Zn₀.₈:S:Sn₀.₂ at different annealing temperatures (A₁).
concentration, segregation of Sn takes place resulting in the increase of resistance. The segregation of Sn dopants at the grain boundary also results in a decrease in the mobility of carriers.

The energy of activation (E_a) for annealed and Sn doped ZnS thin films is measured from the slope of the log of resistivity with the reciprocal of temperature by the following equation:

\[ E_a = \frac{d(\ln(\rho))}{d(1000/A_T)} \]

where \( \rho \) and \( A_T \) stand for resistivity and annealing temperature, respectively. Table 5 shows that the energy of activation of ZnS thin films increases with the amount of Sn incorporation and annealing temperature. Due to the increased carrier concentration and decreased dislocations caused by Sn contents or by high-temperature annealing, localized carriers dominate in the bulk states of ZnS lattice that require higher energy to replace an interstitial atom and excite the bulk states. The higher energy requirement in the interstitial sites increases the value of activation energy.

4. Conclusion

In this work, we report the effects of annealing temperature and doping concentration on the structural, optical and electrical properties of Zn_{1-x}S:Sn_x thin films prepared by the chemical bath deposition method. High level of Sn doping content and high temperature annealing reduce lattice constant, micro-strain, dislocation density and intrinsic stress but increase the crystallite size due to larger compressive stress and lower average tensile elastic stress. Optical parameters like transmission coefficient, depth of penetration, bandgap, steepness parameter and absorption edge wavelength are increased whereas absorption coefficient, Urbach energy, refractive index and dielectric constant are reduced with the amount of Sn content and annealing temperature. Electrical properties of ZnS films are also influenced as Sn doping with high-temperature annealing enhances the value of Hall coefficient, carrier concentration, the energy of activation and resistivity while carrier mobility and current density get reduced due to the grain boundary scattering and the dominant number of localized carriers.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Table 5. Electrical properties of Sn-doped ZnS thin films.

| Doping concentration | Annealing temperature (°C) | Mobility (cm² VS⁻¹) | Hall coefficient (cm² C⁻¹) | Resistivity (Ω cm) | Carrier concentration (cm⁻³) | Energy of Activation (eV) |
|----------------------|-----------------------------|----------------------|-----------------------------|--------------------|-----------------------------|--------------------------|
| Undoped ZnS          | 150                         | 192.45               | 1.47 \times 10⁶            | 13.52 \times 10⁴   | 4.25 \times 10⁴             | 3.049                    |
|                      | 200                         | 187.64               | 1.63 \times 10⁶            | 14.29 \times 10⁴   | 4.79 \times 10⁴             | 3.436                    |
|                      | 250                         | 184.27               | 1.76 \times 10⁶            | 15.04 \times 10⁴   | 5.11 \times 10⁴             | 3.826                    |
|                      | 300                         | 181.78               | 1.93 \times 10⁶            | 15.31 \times 10⁴   | 5.83 \times 10⁴             | 4.202                    |
| Zn_{0.88}S:Sn_{0.12} | 150                         | 174.24               | 2.24 \times 10⁶            | 18.67 \times 10⁴   | 7.46 \times 10⁴             | 3.186                    |
|                      | 200                         | 172.76               | 2.39 \times 10⁶            | 19.46 \times 10⁴   | 7.94 \times 10⁴             | 3.582                    |
|                      | 250                         | 168.55               | 2.56 \times 10⁶            | 20.54 \times 10⁴   | 8.76 \times 10⁴             | 3.989                    |
|                      | 300                         | 165.83               | 2.72 \times 10⁶            | 21.76 \times 10⁴   | 9.88 \times 10⁴             | 4.403                    |
| Zn_{0.84}S:Sn_{0.16} | 150                         | 160.58               | 2.98 \times 10⁶            | 28.45 \times 10⁴   | 11.84 \times 10⁴            | 3.364                    |
|                      | 200                         | 159.32               | 3.13 \times 10⁶            | 29.89 \times 10⁴   | 12.56 \times 10⁴            | 3.785                    |
|                      | 250                         | 158.47               | 3.25 \times 10⁶            | 31.18 \times 10⁴   | 13.61 \times 10⁴            | 4.207                    |
|                      | 300                         | 157.71               | 3.34 \times 10⁶            | 32.73 \times 10⁴   | 14.72 \times 10⁴            | 4.637                    |
| Zn_{0.80}S:Sn_{0.2}  | 150                         | 153.69               | 3.58 \times 10⁶            | 39.34 \times 10⁴   | 17.24 \times 10⁴            | 3.501                    |
|                      | 200                         | 153.17               | 3.69 \times 10⁶            | 41.45 \times 10⁴   | 18.61 \times 10⁴            | 3.939                    |
|                      | 250                         | 152.88               | 3.82 \times 10⁶            | 44.68 \times 10⁴   | 19.97 \times 10⁴            | 4.395                    |
|                      | 300                         | 152.63               | 3.94 \times 10⁶            | 48.06 \times 10⁴   | 21.16 \times 10⁴            | 4.857                    |
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