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Composition-structure-property relationships in thermally evaporated ZnS thin films and Ag/n-ZnS/FTO Schottky barrier diodes

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Abstract

Nanostructured zinc sulphide (ZnS) thin films were deposited by thermal evaporation under high-vacuum conditions. We systematically investigated how film thickness and substrate temperature affect their structural, optical, and electrical properties. EDS and XPS analyses confirmed a near-stoichiometric to slightly Zn-rich composition, with Zn^{2+} and S^{2-} as the predominant chemical states. Variations in Zn/S stoichiometry correlated with changes in the structural, optical, photoluminescence, and electrical properties of the ZnS films. X-ray diffraction confirmed the formation of cubic ZnS layers with a pronounced (111) preferred orientation and a lattice parameter of 5.396 Å. The 300 nm films deposited at 323 K exhibited a mean crystallite size of ~25 nm, microstrain of 1.45×10^{-3} , and dislocation density of $1.61 \times 10^{15} \text{ m}^{-2}$. The optimized film exhibited n-type conductivity with a mobility of $49.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, a resistivity of $2.35 \times 10^{-2} \Omega \text{ cm}$, and a carrier concentration of $5.38 \times 10^{18} \text{ cm}^{-3}$. The films showed visible-region transparency up to 92%, direct bandgaps of 3.40-3.50 eV, and an absorption coefficient $> 1 \times 10^4 \text{ cm}^{-1}$. Ag/n-ZnS/FTO Schottky diodes exhibited rectifying characteristics, yielding barrier heights of 0.67 and 0.72 eV from I-V and C-V measurements, respectively, an ideality factor of 1.03, and a rectification ratio of 5.95. These findings support the potential of grown ZnS thin films as window/buffer layers in photovoltaic cells and in Schottky-barrier electronic applications.

Keywords: Nanostructured thin films, Zinc Sulphide, bandgap tuning, Schottky diode, Wide-bandgap semiconductor, II-VI compound semiconductors

1.0 Introduction

Nanostructured semiconductor thin films have emerged as promising materials for the development of diverse nanoscale and multifunctional devices. Their nanoscale dimensions lead to distinctive physical characteristics, such as quantum confinement and an enhanced surface-to-volume ratio. These features significantly influence their optical and electronic behaviour, making such films attractive for applications in advanced optoelectronics, sensing technologies, and energy-conversion systems [1]. Zinc sulphide (ZnS) is an II–VI semiconductor that has attracted considerable research interest because of its favourable optical and electronic characteristics, which make it a promising material for a range of optoelectronic applications. It commonly occurs in two crystalline forms, namely cubic zinc blende (sphalerite) and hexagonal wurtzite. The cubic zinc-blende structure is typically stable under ambient conditions and possesses a direct optical bandgap of approximately 3.54–3.68 eV. In contrast, the hexagonal wurtzite structure is generally favoured at higher temperatures and exhibits a slightly wider direct bandgap in the range of 3.70–3.91 eV. In addition, the relatively large exciton binding energy of about 40 meV enhances the optical characteristics of ZnS, supporting its suitability for optoelectronic applications [2–4]. In the cubic zinc-blende structure, Zn and S atoms occupy a tetrahedrally coordinated arrangement within a face-centered cubic lattice, resulting in comparatively high structural stability [5]. ZnS exhibits high optical transparency across the visible and infrared spectral regions, together with a relatively high refractive index of approximately 2.35 and low optical absorption. These characteristics make ZnS a promising material for a wide range of photonic and optoelectronic applications [6–7]. Furthermore, ZnS offers the advantages of good chemical stability, comparatively low toxicity, and the natural abundance of its constituent elements, making it an attractive alternative to cadmium-based semiconductors such as CdS. Avoiding cadmium, a toxic heavy metal, can also reduce potential environmental and health risks, thereby enhancing the suitability of ZnS for more environmentally sustainable semiconductor applications [6,8]. ZnS has emerged as an environmentally favourable substitute for conventional buffer or window-layer materials used in thin-film photovoltaic structures. The combination of a wide bandgap, high optical transparency, good chemical

stability, and favourable electronic properties makes ZnS a versatile semiconductor with potential for applications in a range of emerging optoelectronic and photonic technologies. In thin-film photovoltaic cells employing $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS) and $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) absorber layers, ZnS is frequently investigated as a buffer/window layer. Its wide bandgap suppresses absorption within the window region, thereby facilitating the transmission of higher-energy photons towards the absorber and potentially limiting carrier recombination losses [7]. Compared with CdS, ZnS's larger bandgap provides improved transparency in the visible spectral range, thereby enhancing photon transmission into the absorber layer [9]. Moreover, favourable lattice compatibility between ZnS and several absorber materials can improve interfacial and device characteristics [10]. The distinctive ultraviolet response of ZnS also makes it a promising candidate for UV photodetection. Its high sensitivity to UV radiation, chemical robustness, efficient photogenerated electron–hole pair production, and stability under demanding environmental conditions are advantageous for applications including flame sensing, optical imaging, and environmental monitoring [11,12]. In addition, the favourable luminescence behaviour of ZnS has supported its use in electroluminescent and photoluminescent systems, LEDs, laser devices, sensors, photovoltaic technologies, photocatalytic applications, bioimaging platforms, and spintronic systems [13]. Despite these advantages, the practical photocatalytic activity of ZnS under visible illumination is constrained by its wide bandgap, which limits its utilization of the visible portion of the solar spectrum. Furthermore, rapid recombination of photogenerated electrons and holes can reduce charge-separation efficiency, thereby lowering the overall quantum yield. Various approaches, including compositional modification and heterostructure formation, have therefore been explored to extend light absorption into the visible region and facilitate more effective charge-carrier separation [12]. The combination of a relatively high refractive index and strong optical transparency also enables ZnS to serve as an antireflection material for optical and infrared window coatings [14]. Moreover, its pronounced chemical stability and resistance to degradation have generated significant interest in ZnS-based photocatalysts for environmental remediation and related applications [15,16]. Recent studies have increasingly explored ZnS as a cadmium-free alternative for photovoltaic applications, particularly as a substitute for conventional CdS buffer layers and as a constituent of ZnS-based alloy systems. This

approach can reduce the environmental and health concerns associated with cadmium while maintaining optical and electronic properties that are favourable for efficient thin-film photovoltaic devices [17]. At the nanoscale, ZnS can exhibit quantum-confinement-related effects arising from its reduced dimensions, creating additional opportunities for tailoring its properties for optoelectronic applications [18]. ZnS-based composite and hybrid buffer layers have also been explored to improve interfacial properties and further enhance photovoltaic device performance [19]. ZnS thin films have been fabricated using a wide range of physical and chemical deposition techniques, including sputtering [20,21], pulsed laser deposition (PLD) [22,23], electron-beam evaporation [24], thermal evaporation [25,26], chemical vapour deposition (CVD) [27], dip coating [28], spray pyrolysis [29], chemical bath deposition (CBD) [8,30,31], and successive ionic layer adsorption and reaction (SILAR) [32]. Among these techniques, thermal evaporation provides an effective route for producing ZnS films with controlled thickness and good surface uniformity. Deposition under high-vacuum conditions reduces the incorporation of atmospheric impurities and limits unwanted oxidation during film growth. The direct conversion of the evaporated material into a condensed solid phase can also promote uniform film formation and satisfactory adhesion to the substrate. Furthermore, the technique can be applied to different substrate materials and offers relatively straightforward control over the deposition rate and film thickness. Its simple configuration, comparatively low processing cost, and scalability make thermal evaporation attractive for fabricating thin films for optoelectronic applications [33]. Although earlier investigations of ZnS thin films have largely concentrated on individual structural, optical, or electrical characteristics [3,13], a comprehensive correlation among these properties under different deposition conditions remains important. In the present investigation, ZnS thin films prepared by thermal evaporation are systematically examined as a function of film thickness and substrate temperature. The effects of these growth parameters on the compositional, structural, optical, morphological, and Hall-effect characteristics are evaluated. Particular attention is given to establishing relationships between growth-dependent changes in composition and structural features and their subsequent influence on the films' optical and electrical behaviour. To further evaluate the electrical characteristics of the optimized ZnS material, Ag/n-ZnS/FTO Schottky barrier

diodes were fabricated and characterized through current–voltage (I-V) and capacitance–voltage (C-V) measurements. These analyses were employed to investigate charge-transport behaviour and the electrical characteristics of the metal-semiconductor interface. The results provide a basis for identifying suitable deposition conditions to enhance crystallinity and electrical transport in ZnS thin films. The optimized films, combining a wide optical bandgap, high transparency, and favourable electrical properties, demonstrate potential for use as window or buffer layers in emerging photovoltaic and optoelectronic technologies.

2.0 Experimental

2.1 Materials

ZnS powder (99.999% purity), procured from Sigma-Aldrich (Merck, USA), was used as the source material for thin-film growth. High-purity indium (In) and silver (Ag), each 99.999% pure and procured from Alfa Aesar (Thermo Fisher Scientific, USA), were used to fabricate ohmic and Schottky contacts, respectively, on the ZnS films. ZnS thin films were deposited on Corning 2947 glass substrates (Corning Inc., USA) and fluorine-doped tin oxide (FTO)-coated glass substrates purchased from Sigma-Aldrich (USA). The FTO-coated substrates were 75 mm × 25 mm, had a sheet resistance of approximately 7 Ω/mm^2 , and an FTO layer thickness of about 150 nm. The refractive indices of the glass and FTO (SnO_2) layers were approximately 1.52 and 1.85, respectively, while the FTO-coated substrates exhibited an optical transmittance of approximately 80–82% across the visible spectral range. During thermal evaporation, molybdenum (Mo) boats were employed as evaporation sources for ZnS, whereas tungsten (W) spiral boats were used for the deposition of In and Ag. A suitably designed physical shadow mask was employed during deposition to define the active area of the ZnS films accurately and to achieve the desired geometry of the metallic contacts on the film surface.

2.2 Methods

ZnS thin films with nominal thicknesses ranging from 100 to 500 nm were deposited on Corning 2947 glass substrates (75 mm × 25 mm) at room temperature (300 K) using thermal evaporation. To examine the influence of substrate temperature, we deposited additional ZnS films with a nominal thickness of 300 nm at substrate temperatures between 323 and 473 K. Before deposition, we cleaned the vacuum chamber sequentially with

trichloroethylene and acetone, then sealed it with vacuum grease (Metroark, India). We deposited the film in a 12A4DM vacuum coating system (HHV, India) at a base pressure of approximately 2×10^{-4} Pa. The ZnS evaporation rate was maintained in the range of 1–3 Å s⁻¹. The source material was evaporated from a molybdenum (Mo) boat positioned approximately 16 cm below the substrate. The substrate holder was continuously rotated at 10–12 rpm during deposition to ensure uniform film coverage. We monitored film thickness *in situ* using a 6 MHz quartz-crystal sensor coupled to a DTM-101 digital thickness monitor (HHV, India). Before deposition, we degreased the substrates, Mo and tungsten (W) boats, and other evaporation-assembly components with 30% hydrogen peroxide (H₂O₂) for 10 min. The components were then ultrasonically cleaned in trichloroethylene, acetone, and methanol (TAM), followed by thorough rinsing with deionized water. Sequential thermal evaporation was then used to fabricate the multilayer structures and metal–semiconductor contacts. For the ohmic-contact configuration, an In/n-ZnS/FTO structure was fabricated by depositing a 300 nm thick n-type ZnS layer on an FTO-coated glass substrate at 300 K. A 200 nm thick indium layer was subsequently deposited through a physical mask with a circular aperture of 1.0 mm diameter, thereby defining the top ohmic contact and its effective contact area. Ag/n-ZnS/FTO Schottky devices were fabricated using 300-nm-thick ZnS films deposited on FTO-coated glass substrates at room temperature (300 K). In these devices, the FTO layer functioned as the rear ohmic electrode, while circular Ag contacts of selected diameters were defined on the ZnS surface using suitable physical masks. A silver layer approximately 200 nm thick was subsequently deposited to form the top metal–semiconductor Schottky contact.

2.3 Characterisations

The structural properties of the ZnS thin films were characterized by X-ray diffraction (XRD) using an X'Pert³ powder diffractometer (PANalytical, Netherlands) operated in the Bragg–Brentano HD geometry. The measurements were performed at 45 kV and 40 mA using Cu K α_1 radiation with a wavelength of 1.5406 Å. Diffraction patterns were recorded

over the 2θ range of 10° – 70° with a step size of 0.03° and a scanning rate of $0.15^\circ \text{ s}^{-1}$ at an elevation angle of 1.7° . The surface morphology was examined using a Supra 55 field-emission scanning electron microscope (FESEM; Carl Zeiss, Germany) operated at an accelerating voltage of 20 kV. Particle-size distributions were determined by statistical analysis of FESEM images using ImageJ software (NIH, USA), with 50 individual particles analyzed per sample. The elemental composition of the deposited films was analyzed by energy-dispersive X-ray spectroscopy (EDS) using an Octane Elect detector (Ametek, USA). Optical transmission spectra were measured in the UV–Vis–NIR spectral region using a UV-3600 spectrophotometer (Shimadzu, Japan) with a slit width of 2 mm. Photoluminescence (PL) spectra were recorded using an RF-6000 fluorescence spectrophotometer (Shimadzu, Japan) with an excitation wavelength of 335 nm, while the emission spectra were collected over the 200–900 nm range. The vibrational properties of the films were investigated by Raman spectroscopy using an inVia microscope (Renishaw, UK) equipped with a 532 nm laser source. The chemical states and surface composition were examined by X-ray photoelectron spectroscopy (XPS) using a Nexsa Surface Analyzer (Thermo Scientific, Thermo Fisher Scientific, USA). The electrical transport properties of the ZnS films were evaluated from Hall-effect measurements using an HMS-5000 system (Ecopia, South Korea) in the van der Pauw configuration. Measurements were performed under an applied magnetic field of 0.56 T using a source current of 1 μA . The measurements were repeated under identical conditions to assess reproducibility, and the reported electrical parameters represent the corresponding mean values for each sample. The electrical performance of the fabricated Schottky barrier diodes was assessed at 300 K through current–voltage (I–V) and capacitance–voltage (C–V) measurements using a 2400 SourceMeter (Keithley) and a 4284A LCR meter (Agilent), respectively. Both instruments were connected to a probe station (Miller Design, USA). Only devices exhibiting reproducible I–V and C–V characteristics were considered for determining and analyzing the relevant diode parameters. Data processing, quantitative analysis, and graphical presentation were carried out using Microcal Origin 8.5 (OriginLab, USA).

The structural characteristics of the ZnS thin films were investigated by X-ray diffraction (XRD) using a powder diffractometer X'Pert³ (PANalytical, Netherlands) configured in the Bragg–Brentano HD geometry. The instrument was operated at 45 kV and 40 mA with Cu K α_1 radiation at a wavelength of 1.5406 Å. Diffraction patterns were acquired over a 2θ interval of 10°–70°, using a step interval of 0.03° and a scanning rate of 0.15° s⁻¹ at an elevation angle of 1.7°. The surface morphology of the films was examined using a field-emission scanning electron microscope (FESEM), Supra 55 (Carl Zeiss, Germany), operated at an accelerating voltage of 20 kV. Particle-size distributions were obtained by statistical analysis of the FESEM micrographs using ImageJ software (NIH, USA). Fifty individual particles were considered for the size analysis of each sample. The elemental composition of the deposited layers was determined by energy-dispersive X-ray spectroscopy (EDS) using an Octane Elect detector (Ametek, USA). Optical transmission measurements were carried out in the UV–Vis–NIR region using a UV-3600 spectrophotometer (Shimadzu, Japan), employing a slit width of 2 mm. Photoluminescence (PL) measurements were performed with a fluorescence spectrophotometer RF-6000 (Shimadzu, Japan) using an excitation wavelength of 335 nm and collecting emission over the 200–900 nm range. The vibrational spectra of the films were examined by Raman spectroscopy using an inVia microscope (Renishaw, UK) equipped with a 532 nm excitation laser. X-ray photoelectron spectroscopy (XPS) analysis was performed using a Thermo Scientific Nexas surface analyzer (Thermo Fisher Scientific, USA). The electrical transport properties of the ZnS films were determined from Hall-effect measurements performed with an HMS-5000 (Ecopia, South Korea) system in the van der Pauw configuration. Measurements were conducted under a magnetic field of 0.56 T with a source current of 1 μ A. Measurements were repeated under identical conditions to confirm reproducibility, and the reported electrical parameters correspond to the mean values for each sample. The electrical characteristics of the fabricated Schottky barrier diodes were evaluated at 300 K by measuring their current-voltage (I-V) and capacitance-voltage (C-V) responses using a SourceMeter, 2400 (Keithley) and an LCR meter, 4284A (Agilent), respectively. Both instruments were interfaced with a probe station (Miller Design, USA). Devices displaying reproducible I-V and C-V responses were selected for subsequent extraction and analysis of the relevant diode parameters. Data processing, quantitative

analysis, and graphical representation were performed using Microcal Origin 8.5 (OriginLab, USA).

3.0 Results and Discussion

3.1 X-ray diffraction analysis

The structural properties of ZnS thin films with varying nominal thicknesses (100-500 nm) deposited at room temperature (300 K) and the layers of nominal thickness of 300 nm deposited at different substrate temperatures (323 to 473 K) were investigated using the X-ray diffraction (XRD) technique. Figs. 1(a) and 1(b) show the corresponding XRD patterns of the films. All films exhibit a nanostructured morphology with a predominant (111) diffraction peak, indicating preferential growth along this crystallographic orientation. The diffraction pattern confirms the formation of the cubic zinc-blende phase of ZnS (JCPDS Card No. 00-005-0566). The diffraction peak intensities varied with film thickness (t) and substrate temperature (S_T). The (111) diffraction peak intensity increased with film thickness up to 300 nm. However, the peak intensity decreased in the 400- and 500-nm-thick films [34]. In contrast, the (111) peak intensity varied nonmonotonically as the substrate temperature (S_T) increased. In order to study and analyze the response of the varying peak intensity, the normalized peak intensity ratio (PIR) of the most significant peak (MSP) of the (111) peak of ZnS is calculated by the relation given in Eq. (1) [35]:

$$PIR = \frac{I_{(111)}}{I_{(111)max}} \quad (1)$$

The crystallite size (D) of the (111) peak of ZnS thin films was determined using the Scherrer relation given in Eq. (2) [36]:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (2)$$

Where λ is the wavelength ($=1.5406 \text{ \AA}$) of X-rays, β is the full-width-at-half-maximum (FWHM) of the diffracted peaks, 2θ is the Bragg angle, and k ($=0.94$) is the shape factor.

The recorded full-width-at-half-maximum (FWHM) values reflect Bragg-peak broadening arising from both instrumental factors and sample characteristics. Instrumental broadening in the FWHM values was corrected using a standard silicon sample to adjust the β values of various peaks. The observed β values were corrected using the relation mentioned in Eq. (3) [37]:

$$\beta = [(\beta_{hkl})^2_{\text{measured}} - (\beta_{hkl})^2_{\text{instrumental}}]^{1/2} \quad (3)$$

The corrected FWHM values were then used to calculate the average crystallite size (D).

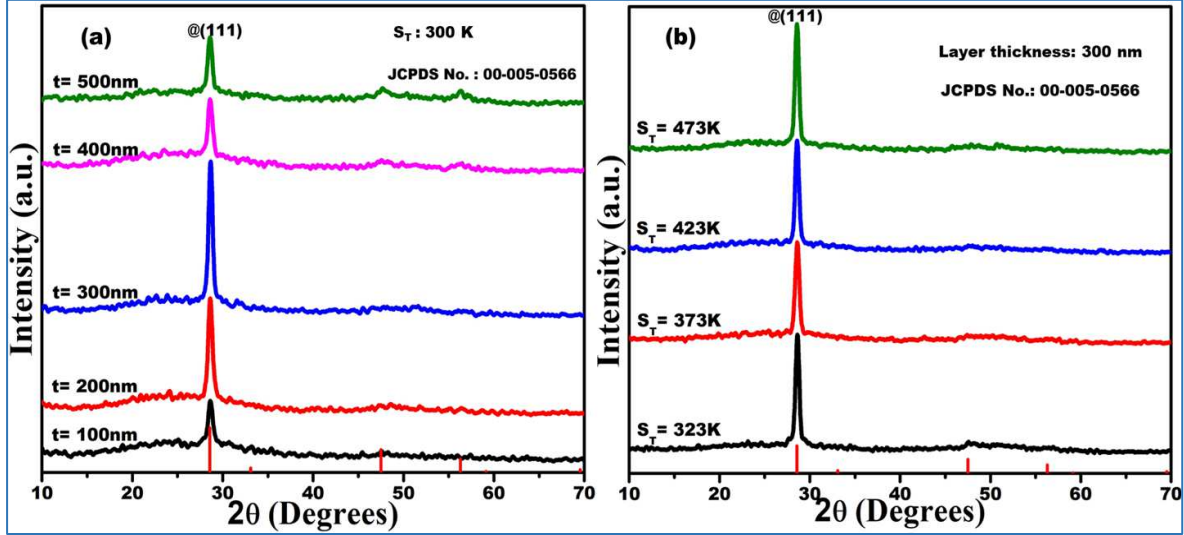


Fig. 1: X-ray diffraction patterns of ZnS films of (a) different thicknesses (100-500 nm) and (b) 300 nm ZnS films as deposited at different substrate temperatures (323 to 473 K).

The normalized peak intensity ratio (PIR) and crystallite size (D) of the (111) peak for ZnS thin films deposited at room temperature with thicknesses ranging from 100 to 500 nm, and for 300 nm thick films deposited at substrate temperatures between 323 and 473 K, are presented in Table 1. As the film thickness increases from 100 to 300 nm, the normalized PIR and D values of the (111) peak increase from 0.39 to 1.00 and from 18 to 24 nm, respectively. The highest PIR and D values are observed for the 300-nm-thick ZnS film (Table 1). This behaviour is attributed to the strong interaction between the incoming vapour atoms and the substrate surface during the initial stages of film growth. As deposition proceeds, the incoming atoms interact predominantly with the previously deposited polycrystalline ZnS layer rather than the substrate. The reduced substrate influence promotes improved crystallographic ordering, resulting in enhanced crystallinity in the 300 nm film [18]. However, both the PIR and D values decrease for films thicker than 300 nm, indicating structural disorder or strain effects at higher thicknesses. Previous studies have reported that crystallite growth becomes limited when the crystallite size approaches the film thickness, a phenomenon known as the specimen thickness effect [38]. The reduction in peak intensity and crystallite size at higher thicknesses is also attributed to the formation of secondary crystallites on the surfaces of the primary crystallites [39].

The 300 nm thick ZnS films exhibit a non-monotonic variation in the PIR and D values as the substrate temperature increases over the range 323-473 K.

Table 1: Structural parameters of the most significant (111) peak of the cubic ZnS phase (a) of different thicknesses as-deposited at room temperature and (b) having a layer thickness of 300 nm deposited at various substrate temperatures (S_T).

Thickness (nm) /Substrate temperature(K)	2θ (Deg.)	Interplanar Spacing (d) (Å)	FWHM (β) (degrees)	Crystallite Size (D) (nm)	Microstrain (ϵ) (1×10^{-3})	Dislocation Density- δ (1×10^{15}) m ⁻²	Intensity (I) (cps)	Peak intensity ratio (PIR)
(a) Substrate temperature: 300 K								
100 nm	28.645	3.113	0.4690	18	1.98	3.00	51	0.39
200 nm	28.630	3.115	0.4613	19	1.95	2.90	94	0.72
300 nm	28.660	3.112	0.3613	24	1.52	1.78	130	1.00
400 nm	28.617	3.116	0.4570	18	1.93	2.84	59	0.45
500 nm	28.594	3.119	0.4552	19	1.92	2.82	54	0.42
(b) Film thickness: 300 nm								
323 K	28.629	3.115	0.3440	25	1.45	1.61	160	0.84
373 K	28.614	3.117	0.4197	20	1.78	2.40	135	0.71
423 K	28.591	3.119	0.3598	24	1.52	1.76	168	0.88
473 K	28.581	3.121	0.3669	23	1.55	1.83	191	1.00
ZnS-JCPDS Card No.– 00-05-0566, system: Cubic, Cell parameter a; b; c = 5.4060 Å, Volume = 157.99 Å ³								

The PIR and D values decrease from 0.84 and 25 nm at 323 K to 0.71 and 20 nm at 373 K, respectively, likely due to increased nucleation. With a further increase in substrate temperature, these values increase to 0.88 and 24 nm at 423 K and to 1.00 and 23 nm at 473 K, respectively. This increase is attributed to enhanced adatom mobility, which promotes grain growth and improves crystallinity. The increase in crystallite size (D) with increasing film thickness (t) and substrate temperature (S_T) is attributed to the coalescence of smaller crystallites into larger ones. Although the PIR reaches its maximum at S_T = 473 K, the higher D value at 323 K suggests a sharper diffraction peak at this S_T . The behaviour indicates an interplay between nucleation rate and surface diffusion during film growth. The FWHM variations follow the t- and S_T -dependent changes in crystallite size within the films.

The interplanar spacing (d) was calculated using Bragg's relation given in Eq. (4) [40]:

$$2d\sin\theta = n\lambda \quad (4)$$

Where λ is the wavelength, n is the diffraction order, and θ is the diffraction angle. Table 1 also presents the calculated d values obtained at different t - and S_T - values. These are found to be lowest for 300-nm films deposited at 300 K, which are attributed to increased grain realignment and stronger interactions between the substrate and vapour atoms [41]. The structural parameters, viz. microstrain (ε), dislocation density (δ), and the number of crystallites (N) of the deposited films were determined using the relations presented in Eqs. (5) - (7) [42]:

$$\varepsilon = \frac{\beta \cos \theta}{4} \quad (5)$$

$$\delta = \frac{1}{D^2} \quad (6)$$

$$N = \frac{t}{D^3} \quad (7)$$

The microstrain (ε) in thin films, which refers to delocalized deformations within the material at the microscopic level, typically results from stress, defects, or thermal vibrations.

Table 2: Unit cell parameter, axis strain, and intrinsic stress along (111) planes of the films of (a) different thicknesses (100 to 500 nm) as-deposited at room temperature (300 K) and at (b) having a nominal thickness of 300 nm deposited at different S_T (323 to 473 K).

Thickness (nm)/Substrate temperature (K)	Axis Strain (%)	a (Å)	Volume-(V) (Å ³)	No. of crystallites (N) (1x10 ¹⁶) m ⁻²	Intrinsic stress (S) (1x10 ⁸) Nm ⁻²
(a) Substrate temperature: 300 K					
100	0.18	5.396	157.11	1.71	1.86
200	0.24	5.393	156.87	2.92	2.40
300	0.29	5.390	156.63	2.17	2.98
400	0.14	5.398	157.31	6.86	1.49
500	0.07	5.402	157.69	7.29	0.74
(b)Thin film thickness: 300 nm					
323	0.19	5.396	157.13	1.92	1.86
373	0.13	5.399	157.38	3.75	1.31
423	0.06	5.403	157.74	2.17	0.56
473	0.02	5.405	157.91	2.47	0.18

The ϵ value decreases from 1.98×10^{-3} to 1.57×10^{-3} as the thickness increases from 100 to 300 nm, suggesting relaxation of lattice imperfections and improved crystalline order [43,44]. Beyond 300 nm, ϵ increases, reaching a maximum at 500 nm, which can be attributed to the buildup of internal stress and defect generation as secondary crystallites grow on primary phases. With increasing substrate temperature, ϵ first increases from 1.454×10^{-3} (323 K) to 1.775×10^{-3} (373 K) and then reduces to $(1.52-1.55) \times 10^{-3}$ at 423-473 K. This trend reflects an interplay between defect formation at intermediate S_T and strain relaxation at higher S_T due to enhanced adatom mobility and improved lattice rearrangement. Dislocation density (δ) refers to the number of dislocation lines per unit volume in a material. It indicates the degree of crystallographic defects and significantly influences the material's mechanical properties [45].

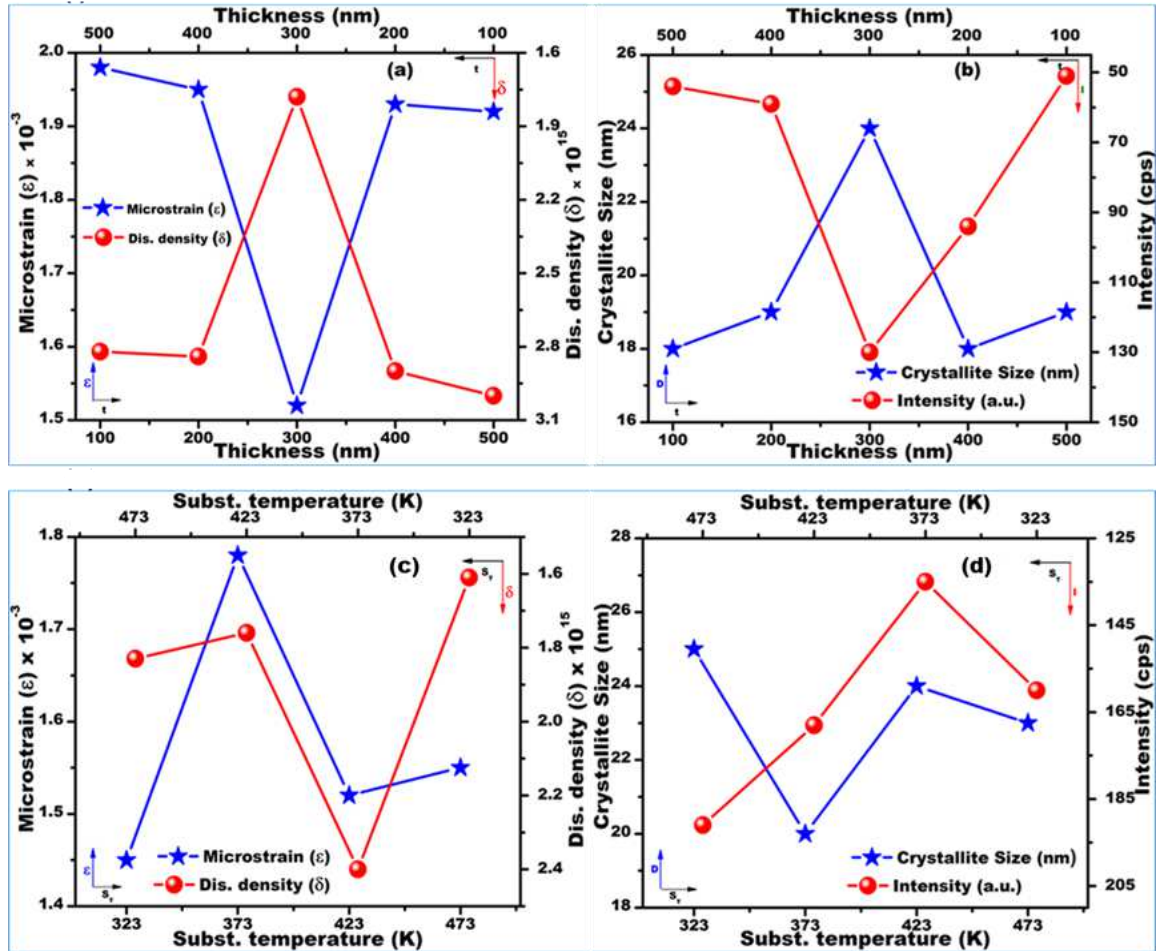


Fig. 2: (a),(c) Variation of micro-strain (ϵ), dislocation density (δ) versus thickness (t) and substrate temperature (S_T) (b),(d), crystallite size (D), intensity (I) versus t and S_T of ZnS thin films

The δ corresponding to the (111) peak of ZnS decreases from $(3.0-1.78) \times 10^{15} \text{ m}^{-2}$ with an increase in t from 100 to 300 nm, indicating improved crystallinity and reduced defect concentration with increasing thickness. For thicker films (400-500 nm), the δ increases marginally $(2.82-2.84) \times 10^{15} \text{ m}^{-2}$, due to the accumulation of internal stress and generation of new defects during prolonged deposition [43,45]. Figures 2(a),(c) illustrate the variations of ϵ and δ with different t (100 to 500 nm) and S_T (323-473 K) values. The number of crystallites per unit area (N) is calculated using the nominal film thickness (t) and the average crystallite size (D), according to the relation presented in Eq. (7). The value of N corresponding to the (111) peak of the ZnS phase decreases for 300 nm, indicating grain coalescence and improved crystallinity. For thicker films (400-500 nm), N increases, which suggests the formation of smaller crystallites due to renewed nucleation and the development of structural defects during prolonged deposition. For the 300 nm ZnS films, N increases from 323 K to 373 K, consistent with reduced crystallite size and enhanced nucleation at intermediate temperatures. At higher S_T (423-473 K), N decreases, reflecting grain growth and improved crystallinity promoted by higher adatom mobility. The unit cell parameters and cell volume for the cubic ZnS structure at different thicknesses and S_T values were calculated from XRD data using the relations given in Eqs. (8) and (9) [46]:

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2} \quad (8)$$

$$V = a^3 \quad (9)$$

The d is the interplanar spacing, h, k , and l are Miller indices, and a , b , and c are the unit cell parameters. The axis strain was calculated using the relationship given in Eq. (10), [47,48]:

$$\epsilon_{zz}(\%) = \left(\frac{c-c_0}{c_0} \right) \times 100 \quad (10)$$

Here, C represents the strained lattice parameter determined from the XRD data along the c -axis, whereas c_0 denotes the corresponding unstrained bulk lattice parameter obtained from JCPDS Card No. 00-05-0566. Table 2 (a,b) presents the variations in c -axis strain with film thickness and substrate temperature. The calculated lattice parameter (a) and unit cell volume (V) of the ZnS thin films were lower than the corresponding bulk values, indicating the presence of compressive strain within the crystallites. This lattice contraction

is attributed to stress arising from the mismatch in thermal expansion coefficients between the film and the substrate, as well as the lattice mismatch at the film–substrate interface [49]. As the substrate temperature (S_T) increases, the lattice parameter and unit cell volume gradually approach the bulk values, while the axial strain decreases, indicating progressive strain relaxation and atomic rearrangement within the lattice. At higher S_T (423–473 K), the stabilization of the lattice parameter and unit cell volume suggests reduced lattice distortion and improved structural quality, resulting from enhanced adatom mobility during film growth. The accompanying increase in interplanar spacing, lattice parameter, and unit cell volume, together with the decrease in axial strain, reflects lattice expansion, reduced compressive strain and defect density, and improved crystallinity. These structural improvements improve the overall electrical and optoelectronic performance of the ZnS thin films.

The behaviour corresponds to the response of other structural parameters. The intrinsic stress can be calculated from Eq. (11) [49]:

$$S = \frac{(c_0 - c)Y}{2c_0\sigma} \quad (11)$$

where Y is the Young's modulus = $8.64 \times 10^{10} \text{ Nm}^{-2}$, and σ is the Poisson's ratio = 0.428 for ZnS, respectively [49]. The intrinsic stress (S) increases from 1.86×10^8 to $2.98 \times 10^8 \text{ Nm}^{-2}$ as the film thickness increases from 100 to 300 nm (Table 2), indicating progressive stress accumulation during the initial stages of film growth. In high-vacuum thermal evaporation, the evaporated species possess considerable thermal energy upon reaching the substrate, and the underlying layers remain exposed to the incoming vapour flux for longer durations as deposition proceeds. The resulting stress is predominantly intrinsic (growth) stress, arising from island coalescence, grain impingement, film densification, lattice distortion, and defect incorporation during film formation [49,50]. In contrast, thermal stress, which arises from the mismatch in coefficients of thermal expansion between the ZnS film and the glass substrate during cooling, is expected to be relatively small because of the moderate substrate temperatures used. Likewise, lattice-mismatch stress is negligible since the films are deposited on amorphous glass, where no epitaxial lattice matching is established. As the film thickness increases to 400 and 500 nm, the intrinsic stress decreases because continued growth facilitates strain relaxation through grain growth, defect annihilation, and grain-boundary rearrangement, resulting in a more relaxed microstructure

with lower residual stress. In contrast, for the 300 nm films, the intrinsic stress (S) decreases monotonically from 1.86×10^8 to $0.18 \times 10^8 \text{ N m}^{-2}$ as the substrate temperature increases from 323 to 473 K (Table 2). This reduction is primarily attributed to enhanced adatom mobility at higher substrate temperatures, which promotes defect reduction and strain relaxation during film growth. Consequently, the lattice parameter and unit-cell volume progressively approach the standard bulk values of ZnS, reflecting a more relaxed crystal structure [51]. Although the crystallite size exhibits a non-monotonic dependence on substrate temperature, the continuous decrease in intrinsic stress indicates that thermally activated atomic diffusion predominantly governs the relaxation of growth-induced intrinsic stress. Any contribution from thermal stress due to cooling is secondary, while lattice-mismatch effects are insignificant due to the amorphous nature of the glass substrate. The structural parameters discussed in this work, including crystallinity, crystallite size, lattice strain, and defect-related characteristics, were evaluated from the X-ray diffraction data using well-established analytical methods widely reported for ZnS and other semiconductor thin films [20,52,53]. The structural parameters discussed above were primarily estimated from the dominant ZnS (111) diffraction peak because the remaining reflections were relatively weak. The subsequent discussion correlates these experimentally determined structural characteristics with the measured optical, electrical, and Schottky diode properties to establish experimentally supported structure–property correlations.

3.2 Raman analysis

Raman spectroscopy is a vibrational characterization technique based on the inelastic scattering of monochromatic light. It provides atomic-level structural insights by identifying molecular vibrations and interactions. This approach is also effective for examining ultrafine structural features of materials [42,54,55]. In this study, Raman measurements of the deposited ZnS thin films were performed using a 532 nm excitation laser over the spectral range of 200–750 cm^{-1} . Figures 3(a) and (b) present the Raman spectra of ZnS thin films with thicknesses ranging from 100 to 500 nm deposited at room temperature (300 K), and of 300 nm films deposited at substrate temperatures between 323 and 473 K, respectively.

The Raman spectra confirm the formation of crystalline ZnS phase and illustrate the evolution of its vibrational characteristics as a function of film thickness and substrate temperature. The prominent bands at 337-352 cm^{-1} are assigned to the first-order longitudinal-optic (LO) phonon mode of cubic ZnS, consistent with previous reports [56]. The band at approximately 436 cm^{-1} is attributed to a combination of LO and acoustic phonons (LO + TA), while the features near 436 and 562 cm^{-1} are assigned to second-order two-phonon processes (2TO-TA and 2TO), and the broad band in the 665-715 cm^{-1} region to second-order 2LO scattering, in agreement with near-resonant Raman studies of ZnS [57-60]. For films deposited at room temperature, the nearly featureless spectrum of the 100 nm film and the weak, broadened Raman bands of the 200 nm film indicate a lower

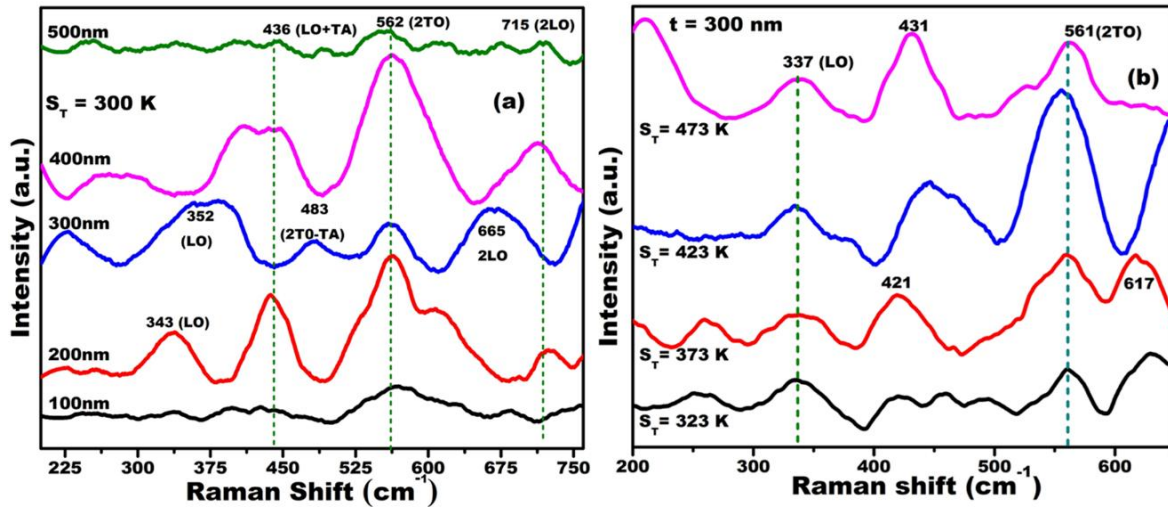


Fig.3: Raman spectra of ZnS thin films of (a) different thicknesses deposited at 300 K and (b) 300 nm thickness deposited at various substrate temperatures

degree of structural ordering than that of the thicker films. In contrast, the LO and multi-phonon bands become progressively more distinct and intense as film thickness increases from 100 to 400 nm, consistent with the increase in crystallite size and diffraction peak intensity observed in the XRD analysis (Table 1). The LO phonon peak shifts from approximately 343 cm^{-1} for the 200 nm film to 352 cm^{-1} for the 300 nm film, corresponding to an increase in crystallite size from 19 to 24 nm and in the XRD peak intensity ratio from

0.72 to 1.00 (Table 1), while coinciding with the maximum optical bandgap of 3.50 eV reported in Table 3.

These observations suggest that the evolution of the Raman vibrational characteristics accompanies improvements in the structural and optical properties of the ZnS films with increasing thickness. However, the Raman results alone do not provide sufficient evidence to establish the underlying mechanism responsible for the enhanced scattering intensity [61,62]. For the 300 nm ZnS films, increasing the substrate temperature from 323 to 473 K modifies the intensity, position, and resolution of the Raman bands. At 323 K, the spectrum is relatively broad, with a prominent band near 561 cm^{-1} , whereas the first-order LO mode near 337 cm^{-1} and the higher-order Raman bands become more distinct at higher substrate temperatures [63-65]. The variation in the intensity and resolution of the Raman bands with increasing substrate temperature is consistent with the structural evolution of the ZnS films revealed by the XRD analysis. Likewise, changes in the intensity and sharpness of the band near 561 cm^{-1} reflect corresponding variations in the films' structural quality. Overall, the Raman results corroborate the thickness- and temperature-dependent structural evolution of the ZnS films observed by XRD while providing complementary information on their vibrational characteristics. Owing to the broad, overlapping Raman bands, quantitative peak fitting was not performed; instead, the Raman observations were interpreted alongside complementary XRD, optical, and electrical characterisation results.

3.3 Optical analysis

Optical characterisation of thin films across the ultraviolet (UV), visible (Vis), and near-infrared (NIR) regions of the electromagnetic spectrum offers valuable insights into their fundamental properties. Analysis of optical spectra yields critical parameters such as the energy bandgap (E_g), refractive index (n), absorption coefficient (α), and extinction coefficient (κ), which are essential for optimising the film's performance in optoelectronic devices [54]. Fig. 4(a) illustrates the transmittance (T%) spectra of ZnS films deposited at room temperature (300 K) with varying thicknesses (t), while Fig. 4(c) shows the T% of 300-nm-thick ZnS films deposited at different substrate temperatures. The measurements were performed over the wavelength range of 200-1000 nm. The transmittance in the visible and NIR regions ranges from 63 to 95%, indicating high optical transparency. Notably, interference fringes observed beyond the absorption edge arise due to multiple

internal reflections at the film/air and film/substrate interfaces, which is indicative of a smooth film surface [54,66]. A sharp absorption edge at 350 nm corresponds to the material's fundamental electronic transition. The high transmission in the visible region, combined with a wide optical bandgap, indicates that ZnS films possess characteristics desirable for window-layer applications in heterojunction solar cells. Additionally, a redshift of the absorption edge observed with increasing thickness can be correlated with improved crystallinity [66]. The absorption coefficient (α) quantifies how deeply light of a specific wavelength can penetrate a material before being significantly attenuated and is defined as the inverse of the penetration depth [42]. The absorption coefficient (α) of the thin film is calculated from the T% using the relation given in Eq. (12) [35]:

$$\alpha = \frac{1}{t} \ln \left(\frac{100}{T\%} \right) \quad (12)$$

Where α is the absorption coefficient, T% is the optical transmission percentage, and 't' is the thin film thickness.

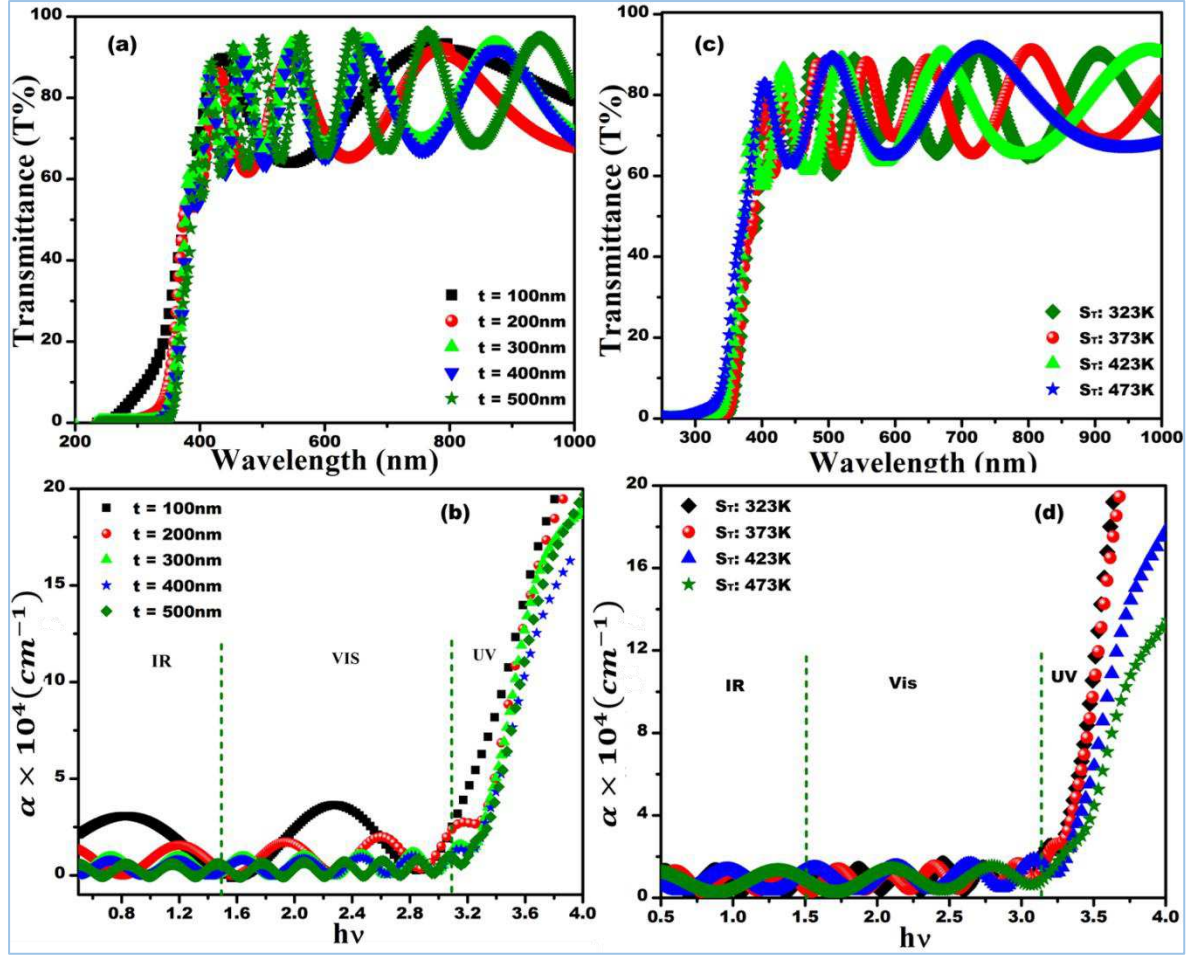


Fig.4 (a),(c): Transmission spectra ($T\%$) versus wavelength (λ) and (b),(d) absorption coefficient (α) versus photon energy ($h\nu$) of ZnS thin films with varying thicknesses (100 to 500nm) and for 300 nm films deposited at different substrate temperatures (323-473 K).

Figs. 4(b),(d) illustrate the variation of the absorption coefficient (α) as a function of photon energy ($h\nu$) for ZnS films of different thicknesses. The ZnS thin films exhibited absorption coefficient (α) values exceeding $1 \times 10^5 \text{ cm}^{-1}$ in the UV region, while values were $1 \times 10^4 \text{ cm}^{-1}$ in the visible region for films of varying thicknesses [49]. The distinct, sharp absorption edges observed in the transmission spectra confirm that the ZnS thin films have a direct bandgap. The optical transition and the energy bandgap of the thin films were determined by analysing the relationship between the absorption coefficient (α) and the photon energy ($h\nu$). A tauc's plot of $(\alpha h\nu)^2$ versus ($h\nu$) yielded a linear region, characteristic of a direct allowed transition. It is widely recognised that the bandgap of semiconductor materials is influenced by various factors, including residual strain, structural defects,

charged impurities, grain-boundary disorder, and quantum confinement effects arising from particle size [25].

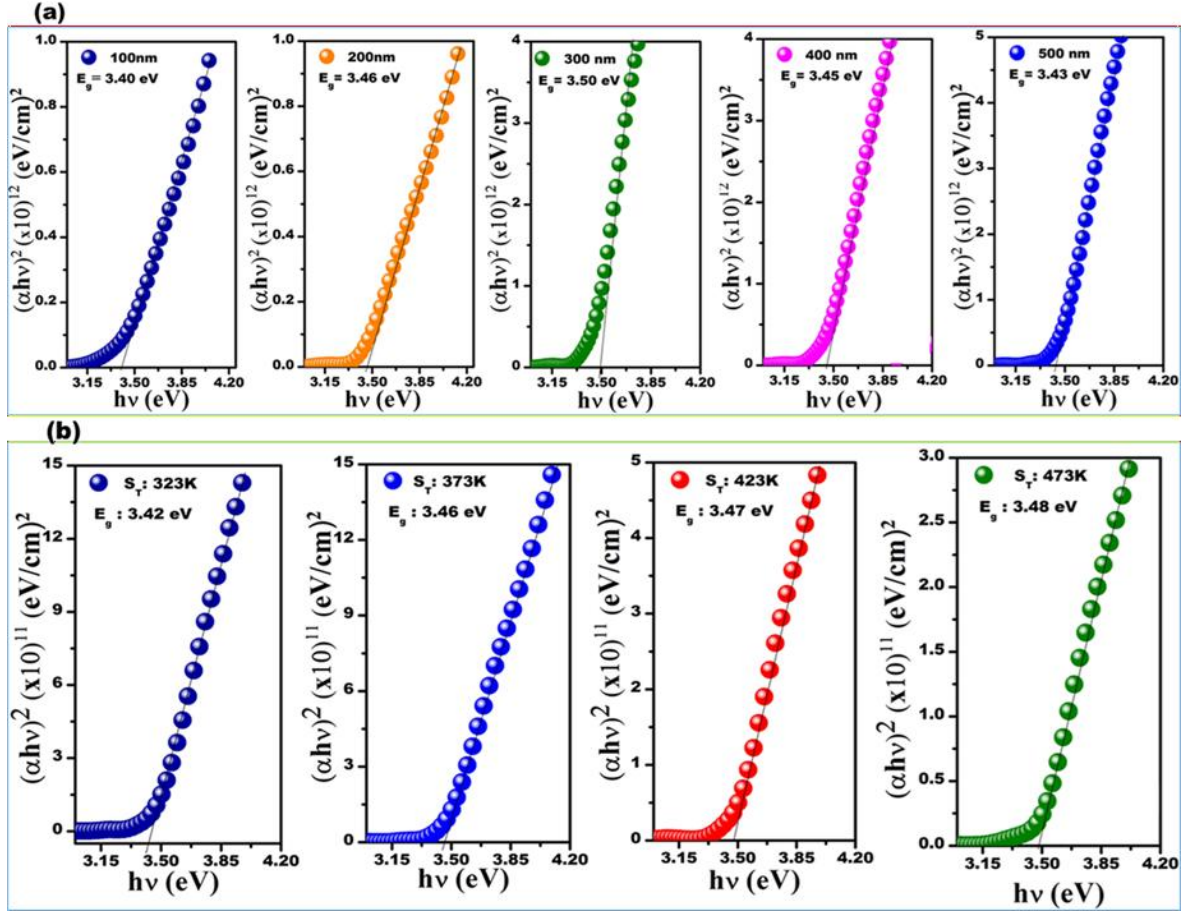


Fig.5 (a) $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) for ZnS thin films with (a) varying thicknesses (100 to 500 nm) and (b) 300 nm films as deposited at different substrate temperatures (323-473 K).

Specifically, tensile strain, which leads to lattice expansion, tends to reduce the bandgap, whereas compressive strain, associated with lattice contraction, typically increases the bandgap [25]. The optical bandgap (E_g) of the thin films was determined using Tauc's relation, as expressed in Eq. (13) [67]:

$$\alpha h\nu = A(h\nu - E_g)^m \quad (13)$$

Where A is a constant, h is Planck's constant, ν is photon frequency, E_g is the optical energy bandgap, and m is the number. The values $m = 1/2$ and $m = 2$ correspond to direct and indirect allowed bandgap transitions, respectively, in the material. In this study, the optical bandgap was observed to vary from 3.40 to 3.50 eV as the film thickness increased from 100 to 500 nm. The E_g first increases from 100 to 300 nm, attains a maximum, and

thereafter decreases with further increases in thickness, i.e., for 400 and 500 nm. This increase in E_g is attributed to improved crystallinity and compressive stress, which is corroborated by the XRD results. The bandgap values calculated for the films are lower than those of bulk ZnS ($E_g = 3.65$ eV), a trend attributed to sulphur deficiency [68]. The variation of E_g with $h\nu$ is illustrated in Fig. 5.

The critical wavelength (λ_c) denotes the maximum wavelength of incident light that can be absorbed by a semiconductor to generate electron-hole pairs. At wavelengths shorter than λ_c , photon energies are sufficient to excite electrons across the material's bandgap, enabling absorption and carrier generation. In contrast, photons with wavelengths longer than λ_c lack sufficient energy to initiate such transitions. The critical wavelength is intrinsically linked to the material's energy bandgap (E_g) as expressed by the relation given in Eq. (14) [38]:

$$\lambda_c = \frac{hc}{E_g} \quad (14)$$

where h is Planck's constant and c is the speed of light. For thermally evaporated ZnS thin films with thicknesses of 100-500 nm, λ_c values range from 353 to 365 nm (Table 3). This variation in λ_c suggests that the optical path difference between reflected beams evolves with film thickness, resulting in corresponding shifts in the interference fringes. The Herve-Vandamme relation, used to calculate the refractive index of ZnS thin films, is presented in Eq. (15) [69].

$$n^2 = 1 + \left(\frac{A}{E_g + B} \right)^2 \quad (15)$$

$A = 13.6$ eV and $B = 3.4$ eV are constants, and n is the refractive index.

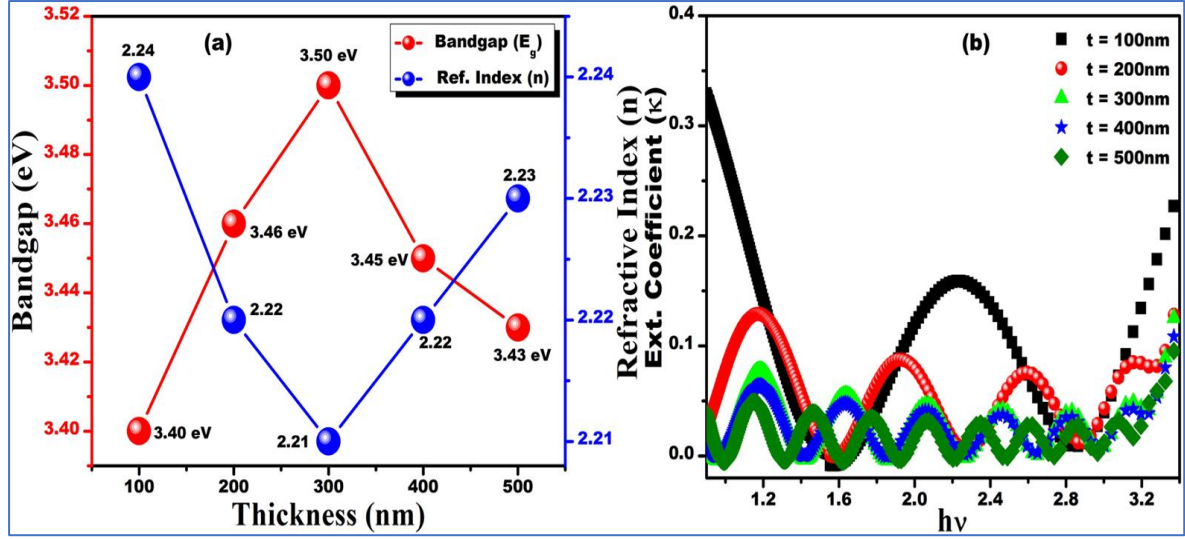


Fig.6: The variations of (a) the optical bandgap (E_g) and refractive index (n) versus thickness, and (b) the extinction coefficient versus photon energy of ZnS films of different thicknesses.

Fig. 6(a) illustrates the variations of the optical bandgap (E_g) and refractive index (n) as a function of thickness.

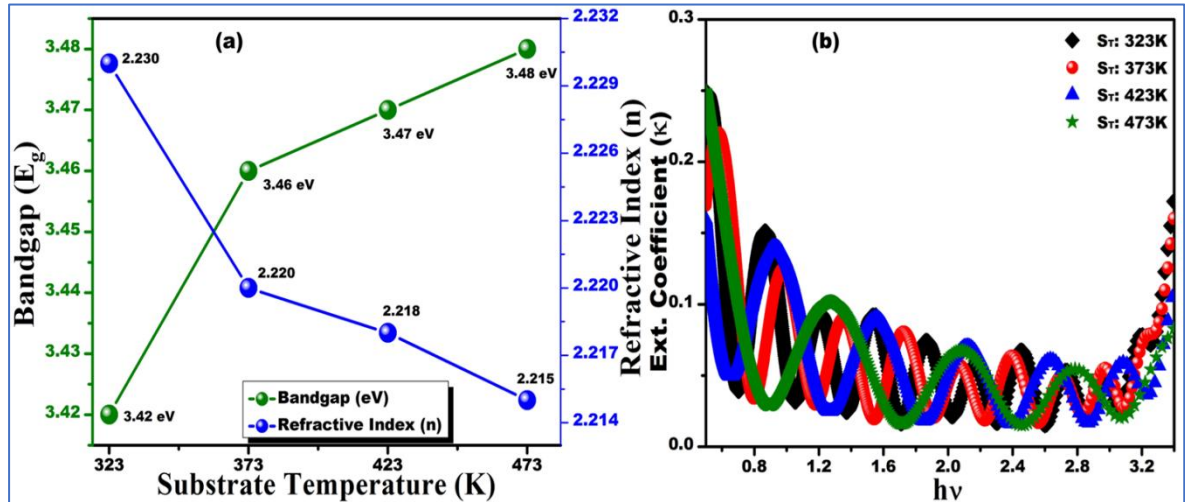


Fig. 7: The variations of (a) optical bandgap (E_g) and refractive index (n) with substrate temperature, and (b) the extinction coefficient with photon energy of ZnS thin films deposited at different S_T values

The refractive index (n) of the thin films ranged from 2.20 to 2.24, with variations likely due to differences in packing density, microstructural changes, and the polarizability of the local field [70]. The refractive index values reported in this study were estimated using the Herve-Vandamme empirical relation, which correlates the refractive index with the optical bandgap and has been widely applied to II-VI semiconductors. Accordingly, the calculated

refractive index values are intended primarily to evaluate the relative variations with film thickness and substrate temperature rather than to provide absolute values. The relation used to calculate the extinction coefficient (κ) for the ZnS thin films is determined by the relation given in Eq. (16) [71]:

$$\kappa = \frac{\alpha\lambda}{4\pi} \quad (16)$$

The extinction coefficient (κ) indicates the optical absorption behaviour of thin films and reflects their surface uniformity and smoothness [70]. It quantifies the material's capacity to absorb incident light at a specific wavelength. The evaluated κ reached a maximum near the absorption edge. Fig. 6(b) illustrates the variation of κ with photon energy ($h\nu$) for ZnS thin films, revealing values below 0.5. Such values of κ suggest minimal light scattering and enhanced internal absorption within the film. A smoother surface minimises scattering losses, thereby promoting more efficient light absorption.

Table 3: The optical parameters of ZnS thin films of (a) different thicknesses (100 to 500 nm) as deposited at room temperature (300 K), and (b) 300 nm films as-deposited at different substrate temperatures (S_T) (323 to 473 K)

Thickness (nm)	T%	Maximum Abs. coeff.(α) $\times 10^5 \text{cm}^{-1}$	Bandgap (E_g)	Ref. Index (n)	Critical Wavelength (λ_c)
(a) Substrate temperature: 300 K					
100	93	1.9	3.40	2.24	365
200	92	2.0	3.46	2.22	359
300	94	1.8	3.50	2.21	354
400	91	1.6	3.45	2.22	359
500	95	2.0	3.43	2.23	361
(b) Film thickness: 300 nm					
323 K	92	1.8	3.42	2.21	354
373 K	92	1.9	3.46	2.22	358
423 K	92	1.7	3.47	2.22	357
473 K	92	1.3	3.48	2.22	356

A slight decrease in κ values was observed with increasing film thickness, indicating a high degree of surface uniformity and smoothness in ZnS thin films. The relatively small bandgap variation (3.40-3.50 eV) suggests that no major modification of the ZnS electronic structure occurs with changes in thickness or substrate temperature. Instead, the observed changes are attributed to the combined effects of strain relaxation, Zn/S stoichiometric variations, and defect-state evolution. EDS results reveal an increasing Zn-rich

composition with thickness, while PL measurements indicate the presence of defect-related states associated with sulphur vacancies and zinc interstitials. These defects can introduce localised electronic states near the band edges, leading to a slight narrowing of the bandgap. Simultaneously, the XRD-derived variations in the lattice parameter and microstrain indicate strain-induced modifications of the electronic band structure. Therefore, the measured bandgap shifts should be interpreted as the cumulative effect of subtle microstructural and compositional changes rather than as evidence of substantial bandgap tuning.

3.4 Morphological and compositional Analysis

Field emission scanning electron microscopy (FESEM) enables high-resolution imaging with enhanced depth of field, making it a powerful tool for detailed surface characterization [45]. It provides critical insights into the surface morphology of thin films, including information on particle size, shape, and spatial distribution [72]. In the present study, FESEM was employed to examine the surface morphology of ZnS thin films, with images captured at a resolution of 200 nm. High-resolution surface and cross-sectional FESEM images and histogram plots of ZnS thin films with varying thicknesses (100-500 nm) are shown in Fig. 8(a-c), and of 300 nm films deposited at different substrate temperatures (323-473 K) are shown in Fig. 9 (a-c). The ZnS films display well-defined, uniformly distributed particles across the surface. Cross-sectional images in Fig. 8(b) indicate that the measured film thicknesses for samples deposited at 300 K, as well as for films with a nominal thickness of 300 nm deposited at different substrate temperatures (Fig. 9(b)), exceed their nominal values. This discrepancy is attributed to uncertainties in the deposition rate and variations in the sticking coefficient.

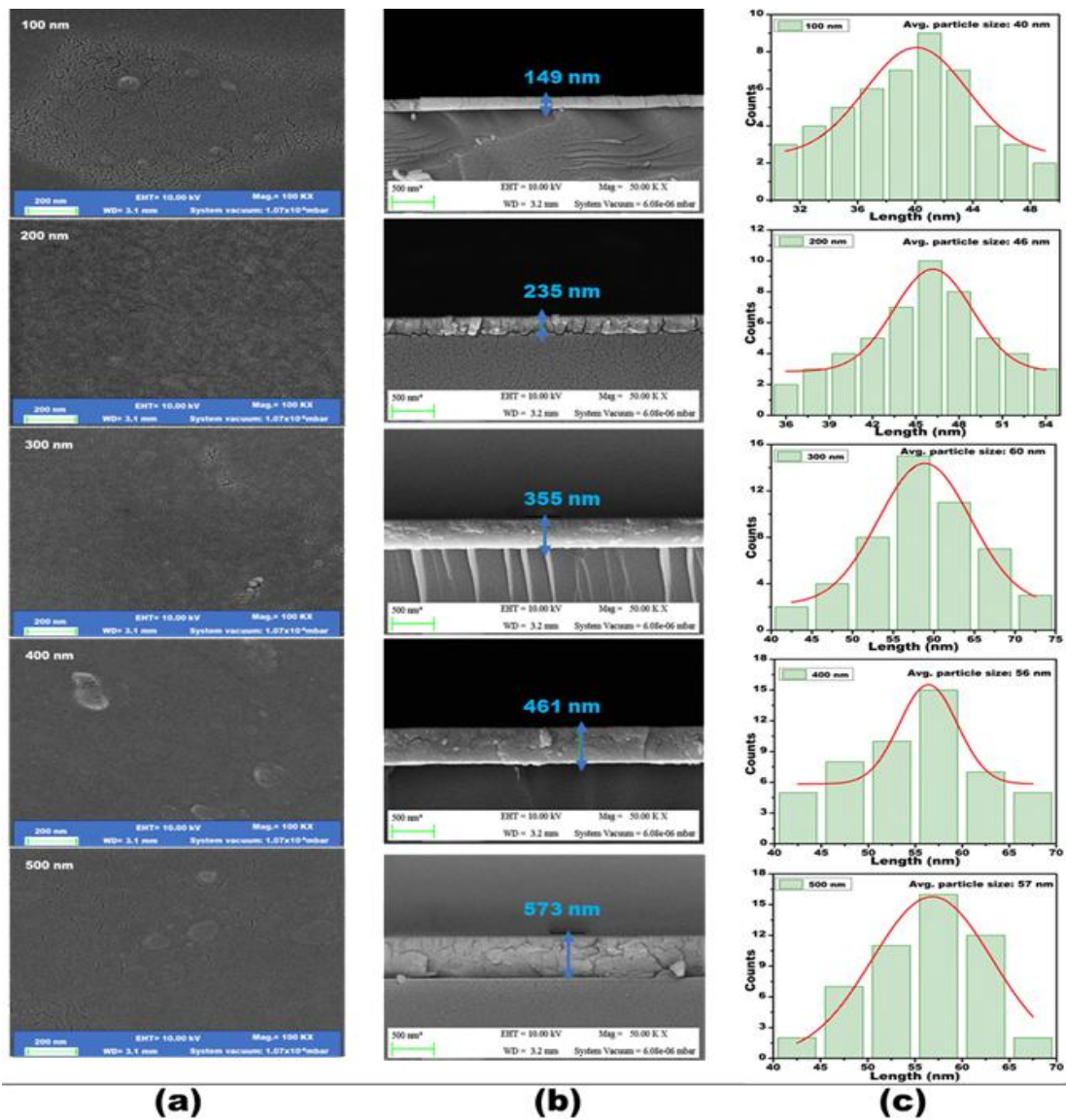


Fig.8: (a) FESEM images, (b) cross-sectional view, and (c) histogram plots showing the average particle size of ZnS thin films with varying thicknesses (100 to 500 nm) as deposited at 300 K

The histograms in Fig. 8 (c) and Fig. 9 (c) show the average particle size in the 40 to 60 nm range, obtained at different thicknesses (100 to 500 nm) and for 300 nm films deposited at various S_T values (323–473 K), as tabulated in Table 4. The particle-size distribution was obtained from the FESEM images using ImageJ. The resulting histograms were fitted with a Gaussian distribution to determine the average particle size and its standard deviation. Owing to the limited number of well-resolved particles in the FESEM micrographs, the analysis was confined to an average of approximately 50 particles. The average particle size determined by FESEM (40–60 nm) is substantially larger than the crystallite size

estimated by X-ray diffraction (XRD) (18-25 nm). This disparity indicates that the particles observed on the film surface are agglomerates consisting of multiple coherently diffracting crystallites [59]. This difference suggests the presence of internal crystallite boundaries within individual grains. However, at the optimum film thickness (300 nm) and substrate temperature (323 K), the formation of larger and more compact grains reduces effective grain-boundary scattering. As a result, carrier mobility increases, while electrical resistivity decreases. Furthermore, the decrease in grain-boundary density and defect concentration improves optical transparency by minimising light scattering and non-radiative recombination centres, thereby enhancing the overall structural and optoelectronic quality of the ZnS films.

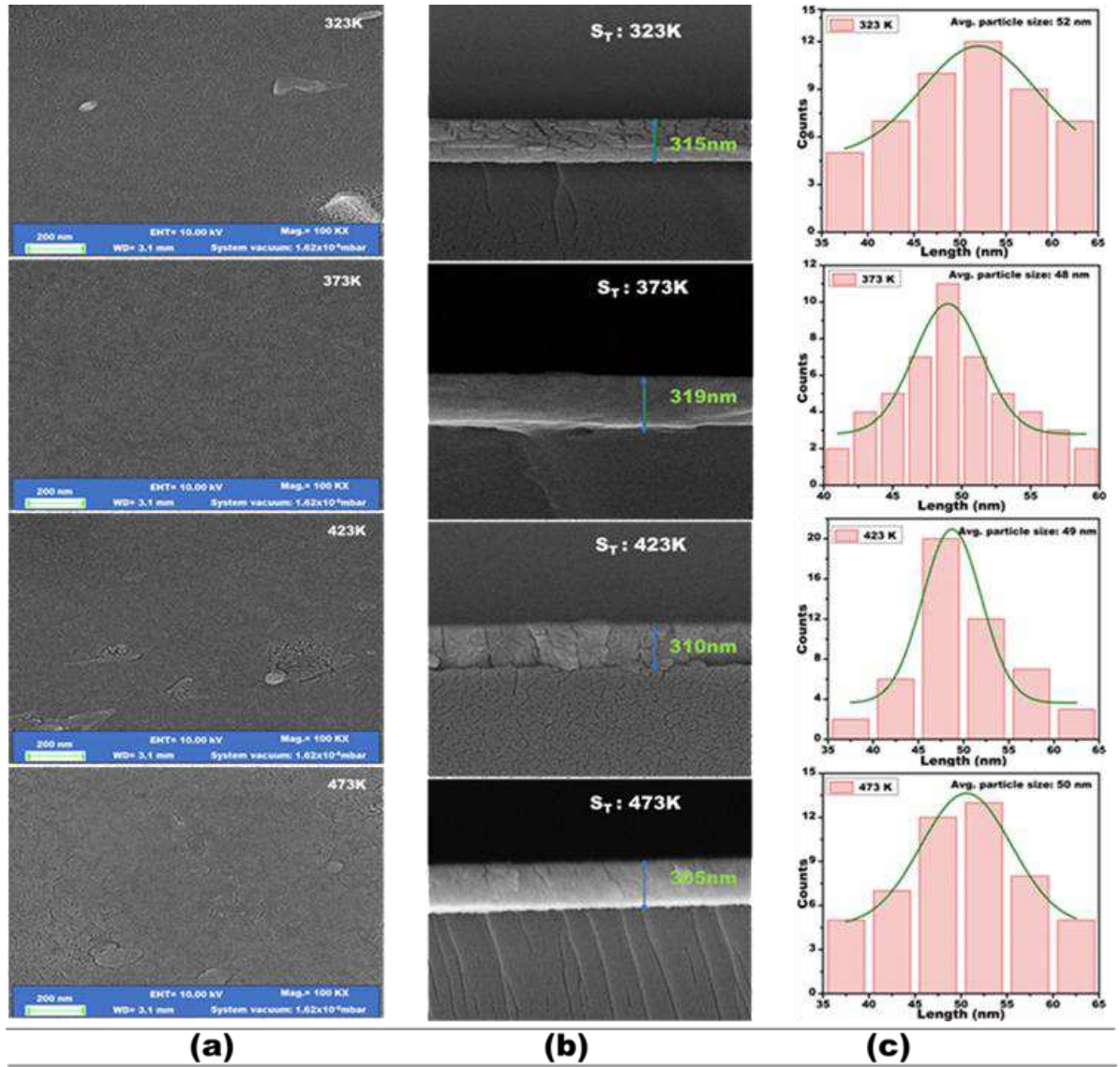


Fig. 9: (a) FESEM images and (b) cross-sectional view and (c) histogram plots showing the average particle size of 300 nm ZnS thin films obtained at different substrate temperatures (323 to 473 K).

The elemental composition of the ZnS thin films was analysed using energy-dispersive X-ray spectroscopy (EDS). The corresponding EDS spectra are presented in Fig.10.

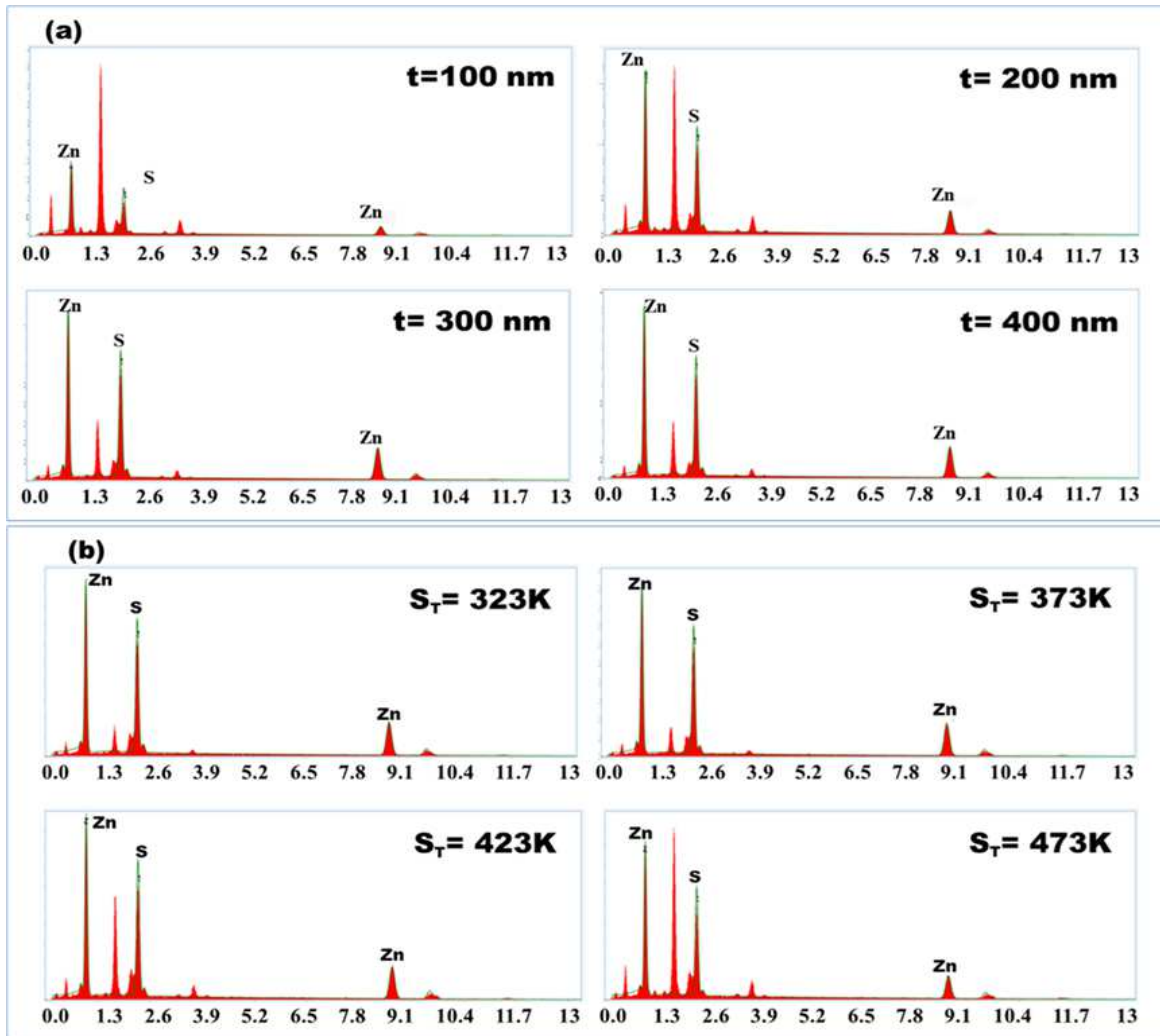


Fig.10: EDS spectra of ZnS thin films of (a) varying thicknesses (100 to 500nm) as-deposited at room temperature and (b) having a thickness of 300 nm as deposited at different substrate temperatures (323-473 K).

The detected elemental peaks confirm the presence of Zn and S in the deposited films, while additional peaks are attributed to the Corning 2947 substrate. Quantitative data on atomic percentages and Zn/S ratios are summarised in Table 4. The analysis reveals that the elemental composition varies with film thickness; the atomic percentage of Zn increases, whereas that of S decreases as t increases. Consequently, the Zn/S atomic ratio for different thicknesses (100 to 500 nm) increases from 0.97 to 1.30, whereas for 300-nm films deposited at various S_T , the ratio varies from 1.26 to 1.05. These compositional variations are primarily attributed to differences in the precursors' vapour pressures during deposition. Near-stoichiometric composition was achieved for the 300 nm thick films deposited at a substrate temperature of 473 K. Increasing the film thickness progressively

shifts the composition from near-stoichiometric to Zn-rich ZnS, whereas increasing the substrate temperature promotes sulphur incorporation and drives the films towards near-stoichiometric composition. These stoichiometric variations induce changes in lattice parameter, intrinsic stress, microstrain, and defect density, which subsequently influence crystallite growth, particle size, Zn-S bonding characteristics, optical transitions, and charge transport behaviour. The increase in Zn/S ratio indicates progressive sulphur deficiency and the formation of donor-like sulphur vacancies (V_S) and zinc interstitials (Zni). These defects contribute to the n-type conductivity by increasing the free-carrier concentration and are also responsible for the defect-related PL emission observed near 668-669 nm. Furthermore, the associated localised defect states influence the slight variations observed in the optical bandgap and electrical transport properties.

Table 4(a,b): EDS data for ZnS films of different thicknesses (100-500 nm) as-deposited at room temperature and 300 nm thick layers deposited at different substrate temperatures (323-473 K).

Thickness (nm)	Elements Atomic (%)		Atomic Ratio	Average particle size (nm)	Stoichiometry
	Zn	S	Zn/S		
(a) Substrate temperature: 300 K					
100	49.3	50.7	0.97	40 ±3	ZnS _{1.03}
200	53.0	47.0	1.13	46 ±2	ZnS _{0.89}
300	55.8	44.2	1.26	60 ±5	ZnS _{0.79}
400	56.1	43.9	1.28	56 ±3	ZnS _{0.78}
500	56.5	43.5	1.30	57 ±6	ZnS _{0.77}
(a) Film thickness: 300 nm					
323	55.2	44.8	1.23	60 ±6	ZnS _{0.81}
373	55.9	44.1	1.26	48 ±2	ZnS _{0.78}
423	54.1	45.9	1.17	49 ±3	ZnS _{0.85}
473	51.3	48.7	1.05	50 ±5	ZnS _{0.94}

3.5 X-Ray photoelectron Spectroscopy (XPS) analysis

X-ray photoelectron spectroscopy (XPS) was employed to confirm the surface chemical composition and oxidation states of the optimized ZnS thin film (300 nm) deposited at room temperature (300 K). Figure 11(a) presents the XPS survey spectrum recorded over the binding energy range of 0-1200 eV, confirming the presence of only Zn and S, with no detectable impurity elements within the detection limit. The broad spectral features observed between 300 and 800 eV are attributed to Zn LMM Auger transitions, while no additional core-level peaks associated with secondary phases or contaminants are detected. The high-resolution XPS spectra of the S 2p and Zn 2p core levels are shown in Figures 11(b) and 11(c), respectively. The Zn 2p spectrum exhibits the characteristic Zn 2p_{3/2} and Zn 2p_{1/2} doublet at binding energies of approximately 1022 and 1044 eV, confirming the Zn²⁺ oxidation state and the formation of Zn-S bonds [73,74]. The S 2p spectrum displays the expected spin-orbit split S 2p_{3/2} and S 2p_{1/2} components, with the dominant S 2p_{3/2} peak centered at approximately 161 eV, characteristic of S²⁻ bonded to Zn. A minor contribution from surface species cannot be ruled out [75]. The Zn 2p and S 2p binding energies are consistent with the reported values for ZnS, and no significant binding-energy shifts are observed, indicating that the chemical environment of Zn and S remains characteristic of Zn-S bonding. Although the relative intensities of the Zn and S core-level peaks qualitatively suggest a slightly Zn-rich surface composition.

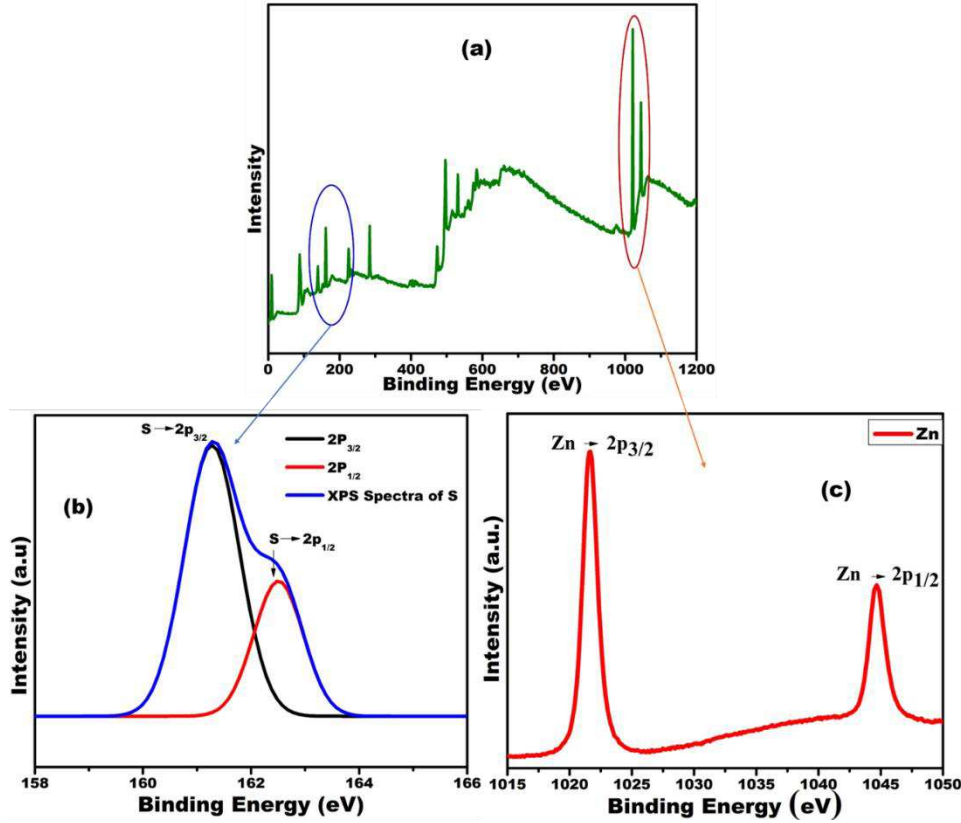


Fig. 11: XPS of ZnS thin films with 300 nm thickness as deposited at room temperature (300 K) showing (a) survey scan; high-resolution spectrum of (b) S 2p, and (c) Zn 2p

3.6 Photoluminescence (PL) analysis

Photoluminescence (PL) describes the light emitted by a material after it absorbs photons. Electrons are promoted to higher-energy states and subsequently return to their ground state, releasing the excess energy as photons in the visible or near-infrared (NIR) region. PL spectroscopy is therefore an incisive technique for interrogating semiconductor optics, revealing band-to-band (BB) transitions, donor-acceptor pair (DAP) recombination, and general carrier-recombination behaviour in thin films [40,76,77]. Fig. 12 displays the PL spectra of ZnS films with nominal thicknesses ranging from 100 to 500 nm, as-deposited at room temperature (300 K), and of 300-nm films deposited at substrate temperatures ranging from 323 to 473 K, all with an excitation wavelength of 334 nm. PL spectra exhibit two peaks at different thicknesses and substrate temperatures. The emission peak at 333-334 nm corresponds to the near-band-edge (NBE) emission of ZnS, arising from the radiative recombination of free excitons or band-to-band transitions.

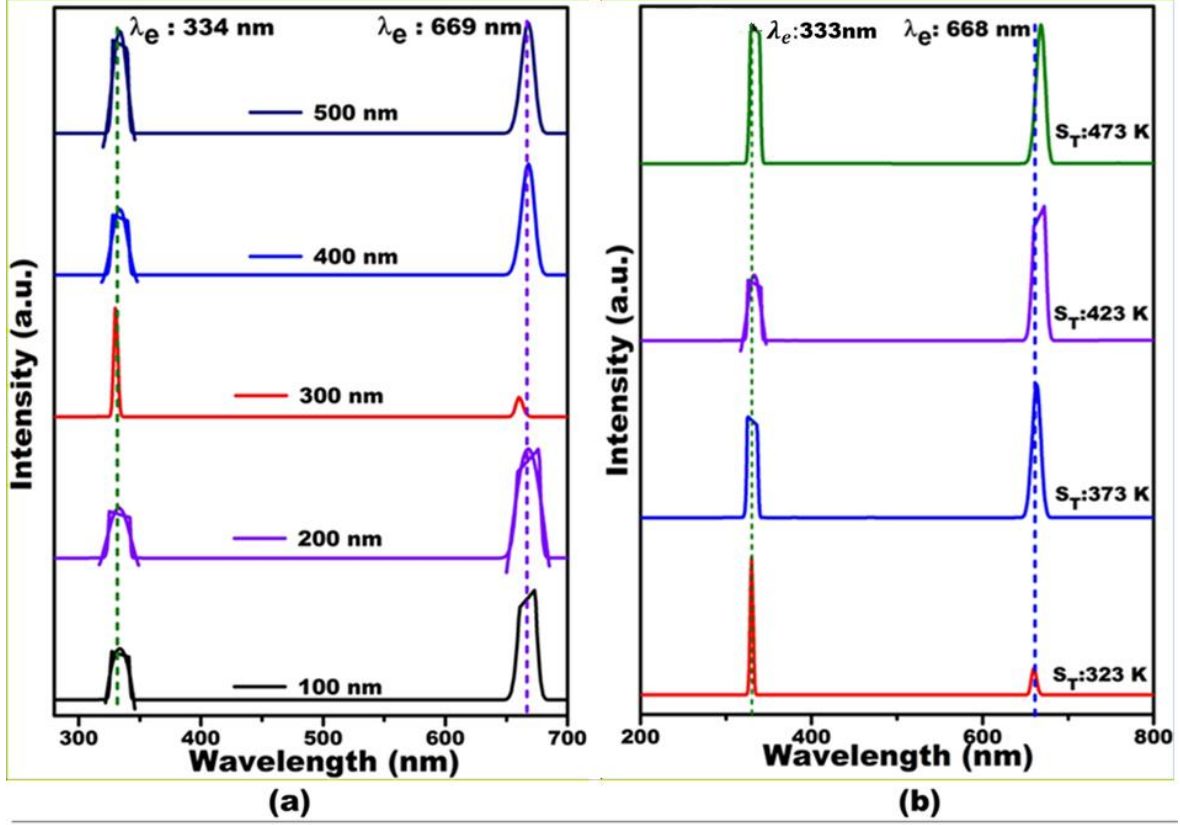


Fig. 12: Photoluminescence (PL) spectra of the ZnS thin films (a) of different thicknesses (100-500 nm) as deposited at room temperature; (b) of 300 nm films as deposited at different substrate temperatures (S_T) (323- 473 K).

This confirms the good optical quality and direct bandgap nature of the deposited ZnS thin films. The visible PL emission at 668-669 nm is associated with intrinsic defects originating from sulphur vacancies (V_S) and zinc interstitials (Zn_i), whose concentration increases with the Zn-rich composition ($Zn/S = 0.97$ -1.30) observed from EDS analysis. The presence of these donor-like defects is further supported by XPS-confirmed Zn-S bonding and n-type carrier concentrations measured by Hall measurements, indicating that the defect-related emission is directly linked to stoichiometry-induced defect states that influence both carrier transport and recombination processes.

3.7 Electrical analysis

The evaluation of electrical properties is essential for assessing the suitability of thin films in electronic device applications. Among the available techniques, the Hall effect is a powerful method for determining the electrical response of semiconducting materials. The measurement is commonly performed using the van der Pauw configuration [78].

The Hall-effect measurements confirmed that all ZnS films exhibited n-type conductivity. The dependence of the electrical resistivity (ρ) and Hall mobility (μ) on film thickness (t) and substrate temperature (S_T) is presented in Fig. 13(a,b), while the corresponding electrical parameters are summarized in Table 5. The ρ increases rapidly from 100 to 400 nm and decreases at 500 nm, while μ rises sharply at 300-400 nm due to improved crystallinity.

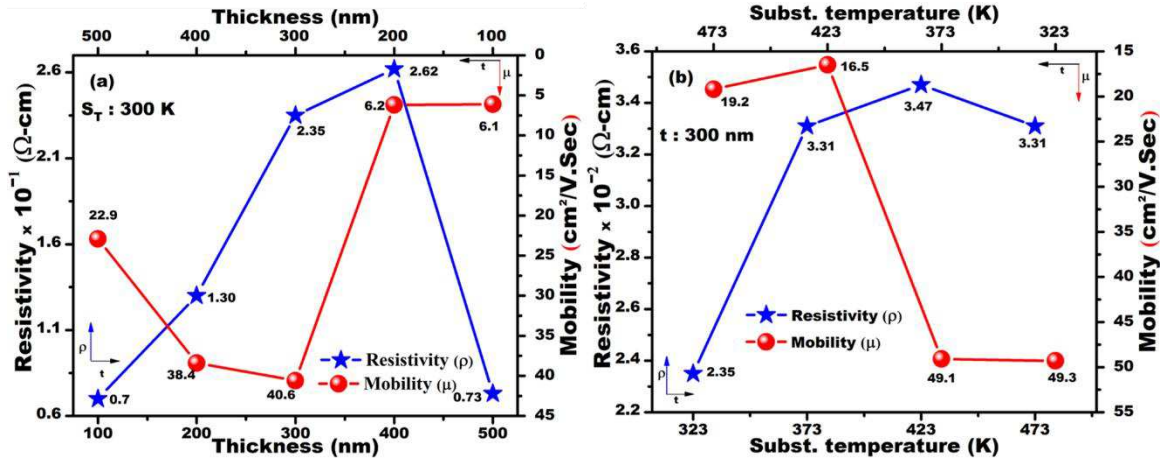


Fig.13: The variation of resistivity (ρ) and mobility(μ) of ZnS films of (a) varying thicknesses (100 to 500 nm) deposited at room temperature (300 K), and (b) 300 nm films as deposited at different substrate temperatures (323-473 K).

N_D decreases at intermediate thicknesses (300-400 nm), indicating reduced defects. For 300 nm films deposited at different substrate temperatures (S_T), resistivity increases with S_T , whereas μ and N_D exhibit non-monotonic variations due to temperature-dependent defect formation. Although the Hall mobilities of the films deposited at 323 K ($49.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and 373 K ($49.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) are nearly identical, this does not necessarily imply comparable microstructural characteristics. The carrier mobility is determined by the combined influence of crystallinity, lattice strain, dislocation density, carrier concentration, and grain-boundary scattering, rather than by any single structural parameter. The maximum Hall mobility of $\sim 49.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ obtained for the optimised ZnS film is consistent with the upper end of values reported in the literature for thermally evaporated ZnS thin films prepared under optimised deposition conditions [79,80].

The 300 nm film deposited at 323 K exhibits a larger crystallite size, lower microstrain, and reduced dislocation density, which collectively minimise carrier scattering at structural imperfections and grain boundaries, thereby facilitating efficient charge-carrier transport.

In contrast, the film deposited at 373 K exhibits increased nucleation and a lower carrier concentration, which compensate for its comparatively less favourable microstructure and result in a similar effective mobility. Increasing the film thickness and substrate temperature enhances adatom mobility, promoting stress relaxation and improved lattice ordering. Consequently, the reductions in microstrain and crystalline imperfections improve the structural quality of the films. These changes subtly modify the electronic band structure, leading to the observed variations in the optical bandgap and optical transparency.

Table 5: Electrical parameters of ZnS thin films of (a) different thicknesses (100-500 nm) as deposited at room temperature and (b) 300 nm as deposited at various substrate temperatures (323-473 K)

Thickness (nm)	Resistivity (ρ) (Ω -cm)	Mobility ($\text{cm}^2/\text{V}\cdot\text{Sec}$) (μ)	Carrier Concentration N_D (cm^{-3})	Diffusion Length (L_D) (μm)	Penetration Depth ($1/\alpha$)
(a) Substrate temperature: 300 K					
100	7.06×10^{-2}	6.1	14.6×10^{18}	1.0	53
200	1.30×10^{-1}	6.2	18.3×10^{18}	0.6	50
300	2.35×10^{-1}	40.6	6.53×10^{17}	10	55
400	2.62×10^{-1}	38.4	6.47×10^{17}	7.0	62
500	0.73×10^{-1}	22.9	3.71×10^{18}	5.0	50
(b) Film thickness: 300 nm					
323	2.35×10^{-2}	49.3	5.38×10^{18}	10	55
373	3.31×10^{-2}	49.1	3.84×10^{18}	10	53
423	3.47×10^{-2}	16.5	10.9×10^{18}	4.0	59
473	3.31×10^{-2}	19.2	4.76×10^{18}	8.0	77

The optimal thickness of thin films is generally comparable to the diffusion length (L_D), which represents the average distance that charge carriers can travel before recombining within the material [81]. Conversely, the penetration depth (δ) denotes the distance light can propagate into the film before its intensity diminishes significantly [82]. The relations that govern the diffusion length and penetration depth are presented in Eqs. (17) and (18) [81,82]:

$$L_D = \sqrt{D_p \tau_c} \quad (17)$$

$$\delta = \frac{1}{\alpha} \quad (18)$$

Where $D_p = \left(\frac{kT}{q}\right)\mu_p$ is the diffusion coefficient, and $\tau_c = \frac{\mu_p m_p^*}{q}$ is the charge lifetime from generation to recombination. For the deposited thin films, the calculated L_D values range between 0.5 and 10 μm , whereas the penetration depth (δ) varies from 50 to 80 nm as the annealing temperature (T_A) increases from 373 to 573 K (Table 5). The calculated diffusion length exceeds the film thickness, whereas the penetration depth remains considerably smaller than it. These relationships indicate favourable charge-transport and optical absorption characteristics that may be beneficial for window-layer applications [83]. The reported optimisation is based on the overall balance of structural, optical, and electrical performance, rather than solely on crystallographic orientation.

3.8 Current transport of Ag/n-ZnS/FTO Schottky barrier diodes:

A key characteristic of a metal-semiconductor (MS) junction is the transport of charge carriers across the interface under an applied electric field, which governs whether the contact exhibits rectifying or ohmic behaviour [84].

3.8.1 Ohmic Contact formation on n-type ZnS thin films

Evaluation of ohmic contacts is essential for assessing the suitability of ZnS thin films for electronic device applications, as contact quality influences charge-carrier injection, transport behaviour, and the overall performance of Schottky barrier diodes. Ohmic contacts were established on n-ZnS thin films by depositing indium (In) electrodes onto ZnS films grown on fluorine-doped tin oxide (FTO) coated glass substrate. For the In/n-ZnS/FTO glass structures, the current-voltage (I-V) characteristics were recorded using a two-probe configuration over the voltage range of -1 to $+1$ V. The resulting linear I-V response confirms the formation of an ohmic contact, as illustrated in Figure 14.

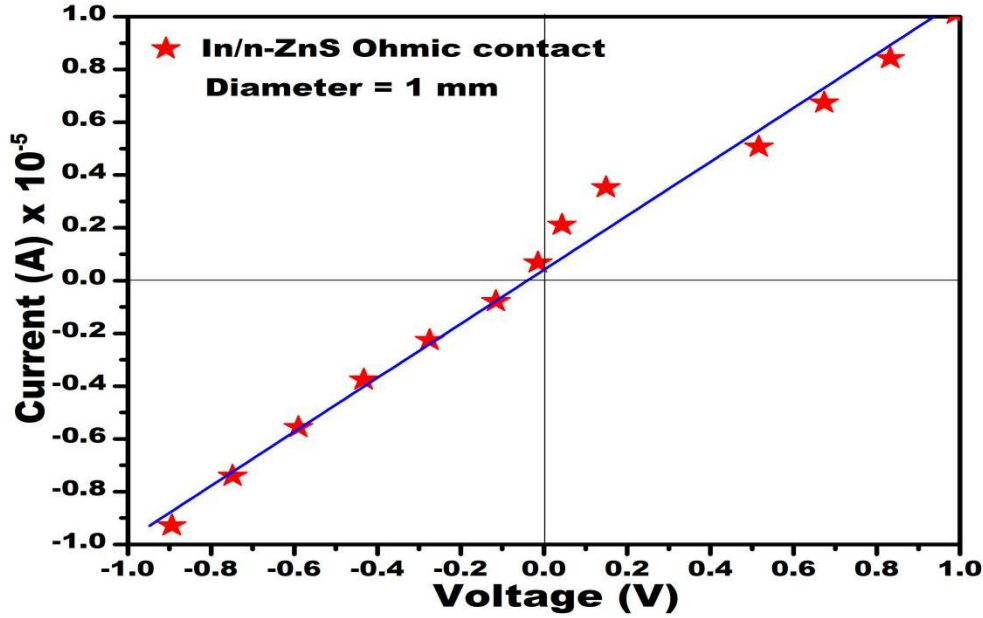


Fig. 14: Current-voltage (*I-V*) characteristics of In/*n*-ZnS ohmic contacts formed on 300 nm thick ZnS films deposited on FTO-coated glass substrates at room temperature (300 K).

The current flowing through the intrinsic film at an applied bias of 1 V was measured to be 1×10^{-5} A. This current magnitude is comparable to values previously reported for ZnS thin films, consistent with earlier studies [9].

3.8.2 Current- voltage (*I-V*) analysis

Metal-semiconductor (MS) junctions have been investigated extensively because of their fundamental significance and widespread applications in electronic devices [85,86]. In Schottky barrier diodes (SBDs), rectification generally occurs when a suitable difference in work function exists between the metal and the semiconductor, resulting in a potential barrier at the interface. Silver (Ag) was chosen as the Schottky contact because of its relatively high work function, excellent electrical conductivity, chemical stability, and compatibility with vacuum deposition processes. Its higher work function relative to *n*-type ZnS promotes the formation of a rectifying Schottky barrier, making Ag an appropriate contact material for investigating charge transport in ZnS-based Schottky barrier diodes. For an Ag/*n*-ZnS Schottky junction, using a work function of approximately 4.6 eV for Ag (Φ_m) and an electron affinity of approximately 3.9 eV for ZnS (χ) yields an ideal Schottky barrier height (Φ_B) of about 0.7 eV, as calculated using the relation given in Eq. (19) [87]:

$$\Phi_B = \Phi_m - \chi \approx 4.6 - 3.9 = 0.7 \text{ eV} \quad (19)$$

Under forward-bias conditions, charge transport across a metal-semiconductor (MS) Schottky barrier diode (SBD) is predominantly governed by the thermionic emission-diffusion (TED) mechanism. For applied voltages satisfying $V \geq 3kT/q$, the diode current is described by the current-voltage relationship given in Eq. (20) [88].

$$I = I_s \left[\exp\left(\frac{qV}{\eta KT}\right) - 1 \right] \quad (20)$$

Here, I_s denotes the reverse saturation current, while J_s represents the corresponding saturation current density, which is calculated using Eq. (21) [46]:

$$J_s = \frac{I_s}{A} = A^{**} T^2 \exp\left(-\frac{q\phi_{bo}}{kT}\right) \quad (21)$$

In Eq. (21), A denotes the diode contact area, and an A^{**} is the effective Richardson constant. A^{**} value of $72 \text{ A K}^{-2} \text{ cm}^{-2}$, previously reported for ZnS, was used in the present analysis [89]. Here, T is the absolute temperature (K), k is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$), q is the elementary charge ($1.6 \times 10^{-19} \text{ C}$), V is the applied forward-bias voltage, ϕ_{bo} is the zero-bias barrier height, and R_s is the series resistance of the diode. The ideality factor (η) quantifies the extent to which the measured I-V characteristics deviate from the behaviour predicted by the ideal thermionic emission-diffusion (TED) model. It is determined using the relation given in Eq. (22) [90]:

$$\eta = \left(\frac{q}{kT} \right) \frac{dV}{d \ln(I/I_s)} \quad (22)$$

In real Schottky barrier diodes (SBDs), the applied voltage is modified to $(V - IR_s)$ to account for the voltage drop caused by the series resistance (R_s). Accordingly, the current-voltage relation is expressed by Eq. (23) [90]:

$$I = I_s \left[\exp\left(\frac{q(V - IR_s)}{\eta KT}\right) - 1 \right] \quad (23)$$

Research on Schottky barrier diodes primarily focuses on understanding their charge-transport mechanisms and improving device performance for applications in high-speed electronics, photodetectors, sensing, and other metal-semiconductor electronic devices. Although Schottky contacts are also employed in certain photovoltaic architectures, the present study focuses exclusively on the electrical characteristics of Ag/n-ZnS/FTO Schottky barrier diodes. Ag/n-ZnS/FTO Schottky barrier diodes with circular contacts of 1 and 2 mm diameter were fabricated by depositing a 200 nm thick Ag layer onto 300 nm thick n-ZnS thin films deposited on FTO-coated glass substrates. Figure 15(a) presents a cross-sectional schematic of the fabricated Ag/n-ZnS/FTO Schottky barrier diode structure, whereas Fig. 15(b) shows the simple current-voltage (I-V) characteristic of a representative device, demonstrating the characteristic rectifying behaviour of the metal-semiconductor junction. The rectifying nature of the Ag/n-ZnS/FTO structure has also been reported earlier [91,92].

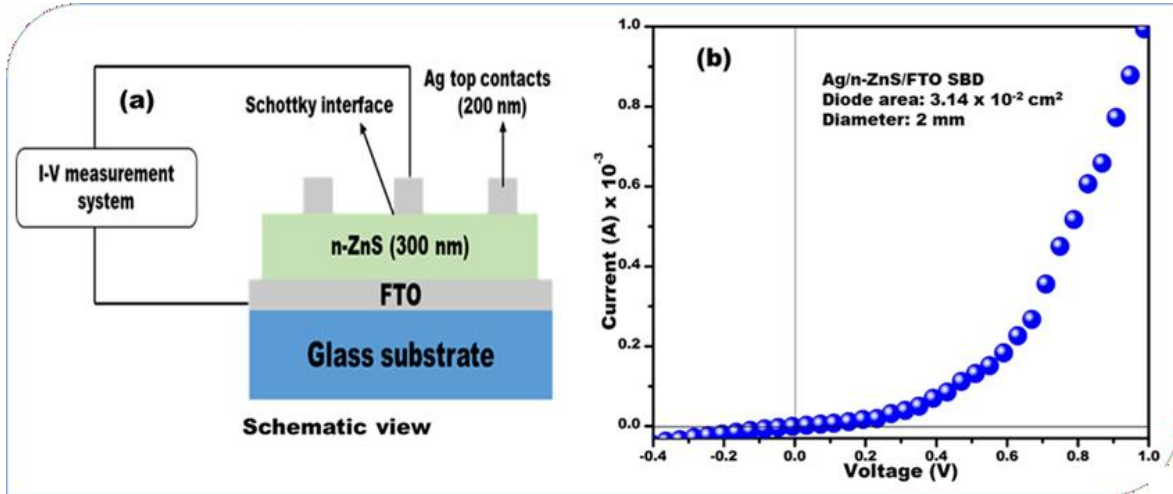


Fig. 15: (a) Schematic illustration of the Ag/n-ZnS/FTO Schottky barrier diode (SBD) structure, and (b) current-voltage (I-V) characteristics of the circular device with a 2 mm-diameter Ag top contact

The forward- and reverse-bias logarithmic current-voltage [$\log(I)$ -V] characteristics of Ag/n-ZnS/FTO SBDs fabricated on n-ZnS thin films with contact diameters of 1 and 2 mm are presented in Fig. 16(a) and (b), respectively. The reverse characteristics of the diode

demonstrate a non-saturating response with bias. The behaviour may be explained by the spatial inhomogeneity of barrier heights (BH) [93,94].

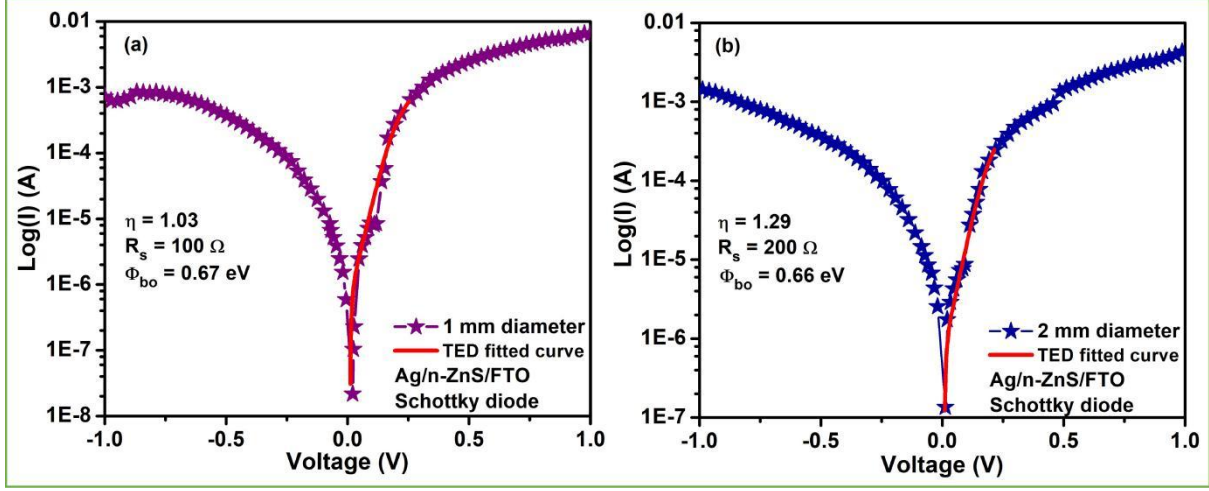


Fig. 16: $\text{Log}(I)$ – V plots of Ag/n-ZnS/FTO Schottky barrier diodes (SBDs) fabricated on n-ZnS thin films with contact diameters of (a) 1 mm and (b) 2 mm

For inhomogeneous MS contacts, the reverse characteristics may be dominated by the current that flows through the low-BH patches. Furthermore, the forward-bias semi-logarithmic current-voltage (I-V) characteristics deviate from linearity at higher applied voltages, indicating the onset of non-ideal transport processes [95,96]. The semi-logarithmic I-V characteristics of the SBDs were analysed using the thermionic emission-diffusion (TED) model. To identify the dominant current-transport mechanism, the experimental current-voltage data were fitted nonlinearly to the TED equation given in Eq. (23) [47,90]. From the fitting results, the principal diode parameters, namely the ideality factor (η), saturation current density (J_s), zero-bias barrier height (ϕ_{bo}), and series resistance (R_s), were determined. The intercept gives the J_s and ϕ_{bo} , while the slope provides η and R_s . The corresponding parameters of the undertaken Ag/n-ZnS/FTO SBDs are presented in Table 6. The rectification ratio (RR) of a Schottky barrier diode (SBD) quantifies its ability to conduct current in the forward direction while blocking current in the reverse direction. It is obtained directly from the current-voltage (I-V) characteristics. Further, the rectification ratio (RR) was calculated as the ratio of the forward current at +V to the magnitude of the reverse current at the corresponding -V, as given by Eq. (24) [97].

$$RR = \frac{|I_F|}{|I_R|} \quad (24)$$

Where I_F is the forward current at a selected positive voltage (+V), and I_R is the reverse current at the corresponding negative voltage (−V)

Table 6: Key parameters of Ag/n-ZnS/FTO circular Schottky barrier diodes with 1 and 2 mm diameters fabricated using 300 nm thin films of n-ZnS, measured at room temperature

Non-linear fitting of I-V curves						C -V characteristics	
Area (cm ²)/diameter	Ideality factor (η)	Current density J _s (A-cm ⁻²)	Barrier height $\phi_{bo, IV}$ (eV)	Series resistance R _s (Ω)	Rectification Ratio (RR) at ± 1 V	Barrier height $\phi_{b,CV}$ (eV)	Donor conc. N _D (cm ⁻³) x10 ¹⁵
7.85x10 ⁻³ (1 mm)	1.03	5.06x10 ⁻⁵	0.67	100	5.95	0.72	3.99
3.14x10 ⁻² (2 mm)	1.29	4.68x10 ⁻⁵	0.66	200	3.04	0.69	2.66

The Ag/n-ZnS/FTO Schottky barrier diodes with contact diameters of 1 and 2 mm exhibited rectification ratios of 5.95 and 3.04 at ±1 V, respectively, confirming the formation of rectifying metal-semiconductor junctions, with the higher ratio of the 1 mm diameter device indicating superior junction quality and more effective suppression of reverse leakage current. The Ag/n-ZnS/FTO Schottky barrier diodes exhibit ideality factors of 1.03 and 1.29, indicating that thermionic emission is the dominant current-transport mechanism for the 1 mm device, while the deviation for the 2 mm device is attributable to interface states, barrier-height inhomogeneity, and a thin interfacial oxide layer at the Ag/n-ZnS interface [98]. The extracted barrier heights of 0.67 and 0.66 eV are close to the theoretical value (~ 0.7 eV) for the Ag/n-ZnS junction, resulting in low saturation current densities of 5.06 x 10⁻⁵ and 4.68 x 10⁻⁵, consistent with efficient carrier blocking under reverse bias [85,86,99]. Furthermore, the measured series resistances of 100 and 200 Ω arise from the combined resistance of the ZnS layer, the metal-semiconductor contact, and the FTO substrate, with the higher resistance in the 2 mm diode reflecting a longer current path and an increased voltage drop. These variations are attributed to surface defects and barrier inhomogeneities at the metal-semiconductor (MS) interface [35,100]. Such

behaviour in Ag/n-ZnS/FTO SBDs with varying contact areas has been reported previously [101-103]. Furthermore, increasing the contact diameter from 1 to 2 mm doubles the series resistance from 100 to 200 Ω and increases the ideality factor from 1.03 to 1.29, indicating enhanced non-ideal current transport due to the larger metal-semiconductor interface and associated resistive effects. Thus, the 1 mm Ag/n-ZnS/FTO Schottky barrier diode exhibits near-ideal rectifying behaviour, characterized by a low ideality factor (1.03), a high barrier height (0.67 eV), and a series resistance (100 Ω), demonstrating a high-quality metal-semiconductor interface and superior electrical performance compared with the previously reported ZnS-based Schottky barrier diode [104].

3.8.3 Capacitance-Voltage (C-V) analysis

The electrical parameters of the metal-semiconductor (MS) Schottky junctions were further evaluated from capacitance-voltage ($C-V$) measurements. For a uniformly doped semiconductor, the junction capacitance can be described by the relation given in Eq. (25) [105],

$$\frac{1}{C^2} = \left(\frac{2}{\epsilon_s q N_A A^2} \right) \left(V_{bi} - \frac{kT}{q} - V \right) \quad (25)$$

where ϵ_s denotes the dielectric permittivity of the semiconductor, N_D is the donor density, V represents the externally applied bias, V_{bi} is the built-in potential, and A is the effective area of the metal-semiconductor contact. The remaining symbols have their conventional meanings.

The donor concentration of the n-type ZnS nanostructured thin films was extracted from the slope of the linear region of the $1/C^2 - V$ characteristics. The corresponding relationship used for determining N_D is given in Eq. (26) [105].

$$N_A = \left(\frac{2}{q \epsilon_o \epsilon_s A^2} \right) \left(\frac{dv}{dc^{-2}} \right) \quad (26)$$

In the present analysis, the relative dielectric constant of ZnS was taken as $\epsilon_s = 8.3$ [106], whereas the permittivity of free space was considered to be 8.85×10^{-14} F cm⁻¹. The capacitance measurements were performed at a frequency of 40 kHz.

The intercept of the linear $I/C^2 - V$ plot with the voltage axis gives the intercept potential V_0 . The built-in potential of the junction was subsequently obtained from V_0 using Eq. (27) [107]:

$$V_{bi} = V_0 + kT/q \quad (27)$$

where T is the absolute temperature, k is Boltzmann's constant, and q is the elementary charge. The parameter V_0 is associated with the energetic separation between the Fermi level and the relevant band edge in the neutral semiconductor region.

The Schottky barrier height determined from the $C-V$ measurements, $(\phi_{b,cv})$, was calculated using Eq. (28) [107]:

$$\phi_{b,cv} = V_{bi} + V_p \quad (28)$$

The potential difference V_p between the conduction-band minimum and the Fermi level was determined from the donor concentration (N_D) using the relation given in Eq. (29) [107].

$$V_p = \left(\frac{kT}{q} \right) \ln \left(\frac{N_c}{N_D} \right) \quad (29)$$

The effective density of states (N_c) in the conduction band, was calculated using Eq. (30) [108].

$$N_c = 2 \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} \quad (30)$$

In this calculation, an effective electron mass of $m_e = 0.24 m_o$ was adopted for ZnS [109].

The resulting values of the $C-V$ derived Schottky barrier height and donor concentration for the devices fabricated on 300 nm thick n-ZnS nanostructured thin films deposited at room temperature (300 K), with different contact dimensions, are presented in Fig. 17, while the corresponding diode parameters are summarized in Table 6. (new)

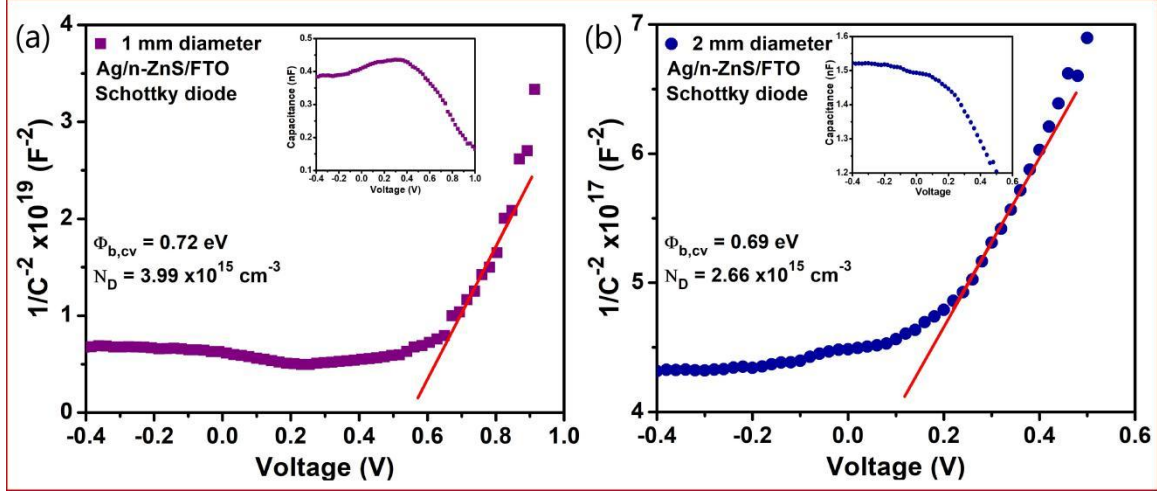


Fig. 17: Reverse-bias capacitance (C^{-2} - V) characteristics of circular Ag/n-ZnS Schottky barrier diodes with contact diameters of (a) 1.0 mm and (b) 2.0 mm, fabricated at room temperature (300 K) and measured at 40 kHz. The insets show the corresponding capacitance-voltage (C - V) characteristics of the corresponding Schottky diodes

Table 6 summarises the Schottky barrier heights obtained from the I - V and C - V analyses, denoted as $(\phi_{bo, I-V})$ and $(\phi_{b, C-V})$, respectively. For all investigated devices, the barrier height derived from the C - V characteristics is higher than the corresponding zero-bias barrier height estimated from the I - V measurements. This difference can be associated with the distinct physical sensitivities of the two characterisation techniques. The C - V method primarily probes the electrostatic properties of the depletion region and is comparatively less influenced by interface-state effects, series resistance, and other non-ideal current-transport mechanisms. In contrast, the I - V -derived barrier height can be affected by these factors, resulting in a comparatively lower apparent barrier height. In contrast, the I - V characteristics are more strongly influenced by interfacial defects and barrier-height inhomogeneities and may also be affected by interfacial trap states or a thin interfacial layer, resulting in an enhanced forward current and, consequently, a lower apparent barrier height. Furthermore, both the I - V ($\phi_{bo, I-V}$) and C - V ($\phi_{b, C-V}$) barrier heights decrease as the metal-semiconductor (MS) interface area increases (Table 6). This behaviour is likely linked with the greater influence of interfacial inhomogeneities and surface roughness over the larger MS interface, which can reduce the effective Schottky barrier height [107,110,111]. The donor concentration obtained from the reverse-bias $1/C^2 - V$ characteristics is lower than the Hall carrier concentration because the C - V method probes

only the ionized donors within the depletion region beneath the Ag/ZnS Schottky contact, whereas the Hall effect measures the average bulk free-electron concentration of the entire ZnS film. Furthermore, the donor concentration extracted from the $1/C^2$ versus V characteristics decreases as the Ag contact diameter increases from 1 to 2 mm. This behaviour is likely associated with the increased influence of interfacial inhomogeneities over the larger metal–semiconductor interface, leading to a lower effective donor concentration extracted from the C - V measurements. The fabricated Ag/n-ZnS Schottky diodes exhibit well-defined rectifying behaviour, confirming the formation of Schottky barriers on FTO-coated glass substrates.

3.9 Structure-property correlations

The thickness-dependent XRD analysis indicates that the 300 nm ZnS films provide a favourable balance between structural quality and electrical transport properties, exhibiting the largest crystallite size, highest carrier mobility, lowest resistivity, and longest carrier diffusion length among the investigated films. The improved structural characteristics are consistent with reduced lattice imperfections and defect-induced carrier trapping, thereby enhancing charge transport. Variations in the lattice parameter and residual strain may also influence the electronic structure and defect distribution, which are consistent with the observed changes in the optical bandgap, absorption edge, and defect-related photoluminescence. The substrate temperature-dependent results reveal two distinct optimization regimes. The films deposited at 473 K exhibit the highest normalized peak intensity ratio (PIR) and a Zn/S atomic ratio closest to unity, suggesting improved crystallographic ordering and compositional uniformity. In contrast, the films deposited at 323 K exhibit the largest average crystallite size, largest particle size, highest mobility, lowest resistivity, and longest carrier diffusion length. These observations suggest that although higher substrate temperatures favour crystallographic texture and near-stoichiometric composition, the films deposited at 323 K exhibit microstructural characteristics more favourable for charge transport. The origin of this behaviour may be associated with differences in stoichiometry, defect distribution, and grain-boundary scattering. Consequently, the optimum substrate temperature differs for structural and electrical performance. The observed variations in stoichiometry and structural

characteristics are reflected in the optical and spectroscopic properties of the ZnS films. Changes in structural imperfections are consistent with the measured variations in the optical bandgap, photoluminescence emission, optical penetration depth, and carrier diffusion length. Likewise, the XPS binding-energy shifts indicate corresponding changes in the Zn-S chemical bonding environment. Collectively, these results suggest that charge-carrier transport is influenced by the combined effects of stoichiometry, lattice strain, and structural imperfections. The redshift of the absorption edge with increasing film thickness is consistent with improved structural quality and may also be influenced by the gradual increase in Zn-rich composition. It may be associated with sulphur deficiency and the formation of donor-like defects, such as sulphur vacancies (V_s) and zinc interstitials (Zn_i), which have been reported to introduce localized electronic states near the band edges. Table 7 compares key parameters of various thin-film materials used as buffer/window layers in photovoltaic cell formations. The present ZnS thin films exhibit high optical transparency, a wide bandgap, moderate mobility, and low resistivity, making them highly suitable as window/buffer layers for photovoltaic applications compared with CdS and In_2Se_3 , which have narrower bandgaps and higher absorption coefficients [36,72]. Additionally, their comparable electrical properties and environmentally benign nature offer advantages over materials such as CdS, while maintaining performance competitiveness with ZnO and ZnSe in photovoltaic applications [35,66,72]. Compared with previously reported ZnS thin films, the present ZnS films exhibit superior electrical performance, evidenced by higher carrier mobility, lower resistivity, and near-ideal Schottky-diode characteristics, thereby demonstrating their enhanced potential for photovoltaic and optoelectronic device applications.

Table 7: Comparison of key parameters of different thin film materials employed as buffer/window layers in photovoltaic cell (PV) applications

Window/ Buffer Material	Thickness (nm)	Annealing Temp. (T _A)/ Substrate Temp. (S _T) (K)	Crystallite size (nm)	Bandgap (eV)	Mobility (cm ² /V-sec)	Resistivity (Ω-cm)	SBD Parameters		Solar Cell Structure	Efficiency (%)
							η	φ _{bo}		
CdS [72,112]	100-500 [72]	300-523 [72] 50-250 [112]	79 [72] 35 [112]	2.27-2.40 [72] 2.42-2.46 [112]	179.8 [72]	50 [72]	4.51 [72]	0.79 [72]	CdS/CdTe [112]	3.76 [112]
ZnO [66]	56-530 [66] 1370 [113]	150-250 [66] 723 [114]	37 [66] 21.5 [125] 19 [113]	3.31-3.44 [66] 3.26 [114] 3.24-3.29 [113]	38.5 [66]	6.2x10 ⁻² [66]	1.93 [114]	0.80 [114]	ZnO/Si [115] CZTS/CdS/ ZnO [113]	14 [115] 13.2 [113]
In ₂ Se ₃ [36,116]	180-270 [36] 80-100 [116]	523-673 [36]	28 [36]	1.92-2.39 [36] 1.7-2.6 [116]	1471 [36]	2.5x10 ⁻² [36]	--	--	CIS/In ₂ Se ₃ / ZnO [116]	8.3 [116]
ZnSe [35]	100-300 [35]	373-573 [35]	20-39 [65]	1.74-2.63 [35]	24-93.3 [35]	1.92x10 ⁻² [35]	1.57	0.97	n-ZnSe/P-Si [117]	2 [117]
In ₂ S ₃ /In ₂ O ₃ [118]	300 nm [118]	523-723 [118]	26/20 [118]	2.34-3.47 [118]	49/228 [118]	1.27x10 ³ / 1.58x10 ⁴	4.83 [119]	0.72 [119]	Al/AZO/In ₂ Se ₃ /p-Si/Al [120]	2.39 [120]
ZnS (Present work)	100- 500	323-473	25	3.40-3.50	49	2.35x10 ⁻²	1.03- 1.11	0.66- 0.69	---	---
ZnS (RF magnetron sputtering/ SILAR/MBE)	150-450 [44]	300 [44]	42-55 [44]	3.69-3.85 [44]	18.40 [121]	2.55x10 ² [121]	1.21 [104]	0.51 [104]	Al/ZnO/ZnS /CIGS/Mo [122]	5.34 [122]

4. Conclusion

Nanostructured ZnS thin films were successfully grown by thermal evaporation under high-vacuum conditions. XRD analysis confirmed that the ZnS thin films exhibit a cubic zinc-blende structure with a preferred (111) orientation. A systematic investigation identified the 300 nm film deposited at 323 K as the optimal sample, exhibiting improved crystallinity, reduced residual strain, enhanced carrier mobility, lower resistivity, high optical transparency, and a wide direct bandgap. Variations in Zn/S stoichiometry, film thickness, and substrate temperature correlated with changes in the structural, optical, photoluminescence, and electrical properties of the ZnS films. The optimized films exhibited a wide bandgap, high optical transparency, and favourable electrical characteristics, while the corresponding Ag/n-ZnS/FTO Schottky barrier diodes showed near-ideal rectifying behaviour and favourable interfacial properties. These results highlight the potential of the optimized ZnS films for window/buffer-layer applications in photovoltaic cells and for Schottky-based electronic and optoelectronic devices.

Data availability statement

All data related to the work undertaken will be made available upon request.

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