

SPRAY-PYROLYSIS ZnSe THIN FILMS WITH TUNABLE OPTOELECTRONIC PROPERTIES THROUGH BORON DOPING AND TEMPERATURE CONTROL

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Abstract

Zinc selenide (ZnSe) is a wide-bandgap II – VI semiconductor with promising applications in photovoltaics, optoelectronics, and photonics. In this study, undoped and boron-doped ZnSe thin films were deposited via spray pyrolysis at substrate temperatures ranging from 250 to 450°C to evaluate the synergistic effects of temperature and dopant incorporation on structural, optical, morphological, and electrical properties. X-ray diffraction confirmed the cubic ZnSe phase with nanocrystalline features, and optimal crystallinity and preferred orientation were obtained at 0.3% B-doping. Optical analyses revealed strong ultraviolet absorption (<400 nm), with transmittance increasing up to 54% at 450°C and a systematic bandgap widening from 3.64 to 3.75 eV, attributed to improved crystallinity and reduced defect density at elevated growth temperatures. Reflectance values remained below 4% across all films, with an exceptionally low value of 0.1% at 350°C, underscoring their potential for antireflection coatings. SEM analysis showed distinct morphology transitions from flower-like structures in undoped films to compact agglomerates upon boron incorporation, enhancing film density. Hall effect measurements indicated that mobility increased with temperature and was further modulated by boron doping, with a balance achieved between conductivity and transparency.

Keywords: ZnSe thin films; Spray pyrolysis; Boron doping; bandgap; X-ray diffraction; SEM

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Introduction

The demand for cost-effective and efficient thin-film semiconductors has skyrocketed with the expansion of solar energy, optoelectronics, and spintronic technologies. Among II - VI semiconductors, zinc selenide (ZnSe) is an attractive candidate due to its wide and direct bandgap (2.7 - 3.7 eV) (Hile *et al.*, 2022), high transparency in the visible-infrared region (Emir *et al.*, 2025), and chemical stability (Liu *et al.*, 2025). These properties make ZnSe particularly suitable for use as buffer/window layers in heterojunction solar cells, as well as in photodetectors, light-emitting devices, and infrared optics (Krishna *et al.*, 2024).

Various methods have been used to deposit ZnSe thin films, including thermal evaporation (Emir *et al.*, 2025; Ke *et al.*, 2021), pulsed laser deposition (Abdalla *et al.*, 2019), chemical bath deposition (CBD) (Khalfi *et al.*, 2023), and vacuum evaporation (Sayeed *et al.*, 2020). Molecular beam epitaxy (MBE) and pulse-laser deposition (PLD) can also produce high-quality crystalline and epitaxial films with excellent control over stoichiometry and interfaces, making them the preferred techniques when atomic-level precision and device-grade material are needed (Arthur, 2002; Pedersen *et al.*, 2024; Shepelin *et al.*, 2023). Although these approaches yield high-quality films, they are often expensive, require sophisticated equipment, and have limited scalability. Chemical bath deposition (CBD), thermal vacuum evaporation, and other solution- or evaporation-based methods are more affordable and easier to implement, but generally offer less control over film microstructure, stoichiometry, and interface abruptness compared to MBE/PLD (Toma *et al.*, 2024). When choosing a deposition method, it is important to consider differences in film quality, scalability, and cost relative to the intended application.

Spray pyrolysis (SP), in contrast, offers a low-cost, scalable, and compositionally versatile route, making it an attractive alternative for large-area photovoltaic applications (Leng *et al.*, 2019; Workie *et al.*, 2023). In SP, an aerosol of precursor solution is sprayed onto a heated substrate, where thermal decomposition yields the film (Deshmukh & Dzade, 2023). The method is particularly attractive for exploratory doping studies because dopant concentration can be adjusted simply through precursor composition and spray parameters, and because films can be deposited on

an inexpensive substrate (Shepelin *et al.*, 2023). The principal limitations of SP include a higher sensitivity of film stoichiometry and microstructure to process parameters, potentially lower crystallinity and film uniformity than MBE/PLD unless carefully optimised, and its somewhat coarse control of atomic-scale interface abruptness.

Recent research has focused on improving ZnSe properties through doping with transition metals, such as manganese (Mn), copper (Cu), and cobalt (Co), or rare-earth ions to tailor the bandgap energy, carrier mobility, and defect states (Bui *et al.*, 2025; Liu *et al.*, 2025). Cu-doping has been reported to modify optical absorption and to reduce the optical bandgap in thin films, which is useful for tailoring absorption edges for optoelectronic applications (Taoufiq *et al.*, 2025). Manganese (Mn) incorporation into ZnSe (Zn, Mn)Se has been extensively studied as a diluted magnetic semiconductor. Mn introduces a localised magnetic moment and can produce giant Zeeman splitting and magneto-optical effects, making (Zn, Mn)Se attractive for spintronic and magneto-optical devices (Sukkabot, 2022). Ni- and Co-doping studies report changes to structural, vibrational, and optical properties, and in some cases emergent magnetic properties and in some cases emergent magnetic responses (Li *et al.*, 2019). Collectively, these works show that relatively small concentrations of transition metals can strongly influence ZnSe's optical and magnetic behaviour, and they establish that controlled doping is an effective route to tune ZnSe properties for specific device targets.

Despite the rich literature on transition-metal doping, light-element doping, and boron doping of ZnSe thin films remains scarcely reported, despite boron's modification of lattice strain. There is theoretical evidence that group I/III impurities and light dopants may modify electronic structure and, in some configurations, can stabilise magnetic order or introduce shallow acceptor/donor levels (Zhao *et al.*, 2022). Work on boron-doped II-VI systems and first-principles studies suggest that boron incorporation could alter carrier concentration and defect chemistry in ways distinct from transition-metal substitution (Fan *et al.*, 2012). Furthermore, the combined effect of deposition temperature and boron doping of ZnSe thin-film properties has not been systematically studied, even though such dual-parameter control is essential for optimising material performance in device-relevant conditions.

In this study, we investigate the deposition of undoped and doped-boron ZnSe thin films via spray pyrolysis at substrate temperatures ranging from 250 to 450°C. We focus on understanding how substrate temperature influences crystallinity, optical transparency, and electronic transport, and how boron incorporation further modifies these parameters. By correlating structural, optical, and electrical properties, we reveal the dopant-temperature interplay as a visible pathway for tailoring ZnSe thin films for optoelectronic and photovoltaic applications. Unlike prior studies limited to a single parameter (dopant temperature only), our work provides mechanistic insight into the synergistic control of ZnSe properties through both deposition temperature and boron doping, paving the way for scalable device integration.

Methodology

Materials and Precursors

Analytical-grade zinc acetate dihydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] and selenium oxide (SeO_2) were used as zinc and selenium precursors, respectively. Nitric acid (HNO_3) served as the complexing agent, while distilled water and isopropanol were employed as solvents. For boron doping, boric acid (H_3BO_3) was added to the precursor solution at molar concentrations of 0.1%, 0.2%, 0.3%, and 0.4%. All reagents were used as received without further purification. Soda lime glass (SLG) slides were selected as substrates due to their availability and thermal stability. Before deposition, the substrates were ultrasonically cleaned in acetone and ethanol, immersed in piranha solution ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$, 3:1 v/v), rinsed in deionised water, and etched in 1 M HCl to remove surface contaminants and alkali residues. The cleaned slides were dried on a hot plate.

Thin Film Deposition via Spray Pyrolysis

Undoped and boron-doped ZnSe thin films were deposited using a computer-controlled spray pyrolysis unit (U-Spray, USP-1500) coupled with a syringe pump for precise solution delivery (Figure 1). The optimised deposition conditions were maintained as follows: a solution flow rate of 1.4 mL over 20 minutes, a nozzle-to-substrate distance of 20 mm, compressed air as the carrier gas, an atomization voltage of +7 kV, and substrate temperatures (T_s) of 250°C, 300°C, 350°C, 400°C, and 450°C. Substrate temperature was monitored and controlled within $\pm 2^\circ\text{C}$ using a K-type thermocouple to ensure reproducibility. Temperature calibration was verified before each run to minimise variations affecting nucleation and

crystallinity. During deposition, the boric acid dopant was dissolved in the main precursor solution containing zinc acetate dihydrate, Selenium dioxide, and nitric acid, as presented in Table 1. The dopant was thus incorporated uniformly into the thin films, allowing precise control over the dopant concentration and distribution. The precursor solution was atomised into fine droplets that were directed towards the heated substrate, where pyrolytic decomposition and chemical reactions occurred to form ZnSe or ZnSe:B. For each deposition condition, the entire 1.4 mL solution was sprayed to ensure uniform film coverage and reproducibility across samples. For clarity, each sample was labelled with an alphanumeric code that reflected both boron concentration and substrate temperature. S1 was a pure ZnSe synthesised with zero boron concentration, serving as a control. S2 was doped with 0.1 boron, S3 was doped with 0.2, S4 with 0.3 and S5 was doped with 0.4 boron concentration. All samples S1 - S5 were deposited at 400°C. However, S6 was a synthesised ZnSe deposited at 250°C, S7 at 300°C, S8 at 350°C, S9 at 400°C and S10 at 450°C.



Figure 1. Setup of a Spray Pyrolysis Machine (USP 1500) and Syringe Pump

Structural and Morphological Characterisation

X-ray diffraction (XRD) was performed using a Rigaku SmartLab diffractometer with Cu K α radiation ($\lambda = 0.154 \text{ nm}$) operated at 40 kV and 30 mA to determine crystallinity, phase purity, and lattice modification due to boron incorporation. The diffraction patterns were recorded between 5° and 80° (2θ) with a step size of 0.01° and a scanning speed of $2.016^\circ/\text{min}$. Phase identification was carried out by comparison with standard JCPDS data, and crystalline size was estimated using the Debye-Scherrer equation below.

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

Table 1. Summary of precursor composition and deposition parameters for ZnSe and B: ZnSe thin films

Sample	Zn(CH ₃ COO) ₂ ·2H ₂ O (mL)	SeO ₂ (mL)	H ₃ BO ₃ (mL)	HNO ₃ (mL)	Vol. dispensed (mL)	Temperature (°C)
S1	1	1	0	0.4	1.4	400
S2	0.9	1	0.1	0.4	1.4	400
S3	0.8	1	0.2	0.4	1.4	400
S4	0.7	1	0.3	0.4	1.4	400
S5	0.6	1	0.4	0.4	1.4	400
S6	1	1	0	0.4	1.4	250
S7	1	1	0	0.4	1.4	300
S8	1	1	0	0.4	1.4	350
S9	1	1	0	0.4	1.4	400
S10	1	1	0	0.4	1.4	450

Where D is the average crystallite size (in nanometers); K is a shape factor, typically around 0.9, which accounts for the shape of the crystallites; λ is the wavelength of the X-rays used (in nanometers); β is the full width at half maximum (FWHM) of the diffraction peak (in radians), which indicates the broadening of the peak due to small crystallite size; and θ is the Bragg angle, which is the angle at which diffraction occurs.

The lattice strain (ϵ) and dislocation density (δ) were also evaluated to assess microstructural imperfections using the relations:

$$\epsilon = \frac{\beta \cos \theta}{4}, \delta = \frac{1}{D^2} \quad (2)$$

where β is the full width at half maximum (FWHM) of the diffraction peak, θ is the Bragg angle, and D is the crystallite size derived from the Debye-Scherrer equation (Mote *et al.*, 2013).

Scanning electron microscopy (SEM, TESCAN MIRA3) was used to study surface morphology, grain distribution, and dopant-induced structural changes. Energy-dispersive X-ray spectroscopy (EDS) was used to quantitatively confirm the elemental composition (Zn, Se, B), and film thickness was measured using a profilometer (Dektak XT, Bruker). The measured film thickness obtained from the profilometer reading was incorporated into the calculation of the absorption coefficient and optical constants, allowing accurate determination of bandgap and refractive index variations.

Optical Characterisation

Optical transmittance and reflectance spectra were recorded in the 200 - 1200 nm wavelength range using an Avantes UV-Vis_NIR spectrophotometer. The absorbance (A) was obtained using the Beer-Lambert law as shown in equation 3 (Hasaneen *et al.*, 2020).

$$A = -\log T = \log \frac{I_0}{I} \quad (3)$$

where T is the transmittance and I_0 and I are the incident and transmitted light, respectively.

The absorption coefficient (α) was calculated from the Lambert equation 4 below.

$$\alpha = 2.303 \frac{A}{t} \quad (4)$$

where t represents the film thickness.

The photon energy (E) was determined using Max Planck's expression, as shown in equation 5.

$$E = \frac{hc}{\lambda} \quad (5)$$

where h is Planck's constant, c is the speed of light, and λ is the wavelength of the incident photon. Finally, the optical bandgap energy (E_g) was estimated from Tauc's relation (equation 6) for direct allowed transitions by extrapolating the linear portion of the $(\alpha h\nu)^{1/n}$ versus $h\nu$ plot to intersect the energy axis (Chinnasamy *et al.*, 2022).

$$(\alpha h\nu)^{1/n} = A^{1/n}(h\nu - E_g) \quad (6)$$

The number $n = 2$ denotes a direct band gap transition, and $n = \frac{1}{2}$ denotes an indirect band gap transition. For the determination of the band gap, the direct ($n = 2$) transitions were considered.

Raw transmittance and reflectance data were corrected for baseline drift and smoothed using a 5-point moving average filter before optical parameter extraction to minimise instrument-induced oscillations and ensure physical consistency.

The refractive index (n) and extinction coefficient (k) were determined from the reflectance and transmittance (T) spectra using the relations of Hasaneen *et al.* (2020) below:

$$n = \frac{(1+R^{1/2})^2 - T^{1/2}}{(1-R^{1/2})^2 - T^{1/2}} \quad (7)$$

$$k = \frac{\alpha \lambda}{4\pi} \quad (8)$$

Electrical Characterisation

Electrical properties (electrical resistivity, carrier type, carrier concentration, and Hall mobility) were measured using an ECOPIA HMS-3000 Hall effect measurement system under room-temperature conditions.

Results and Discussion

XRD Analysis

XRD patterns of undoped (Figure 2) and boron-doped ZnSe (Figure 3) films deposited at a substrate temperature of 400°C confirmed the polycrystalline nature of the samples, with diffraction peaks corresponding to the cubic ZnSe phase (JCPDS card no. 01-073-1764).

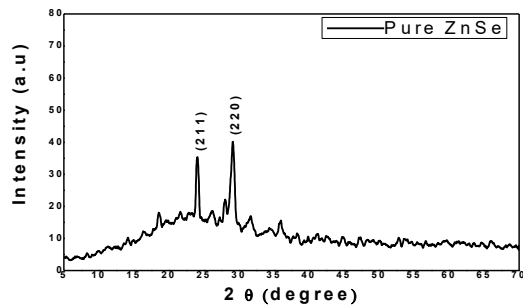


Figure 2. X-ray Diffraction Pattern for Undoped ZnSe

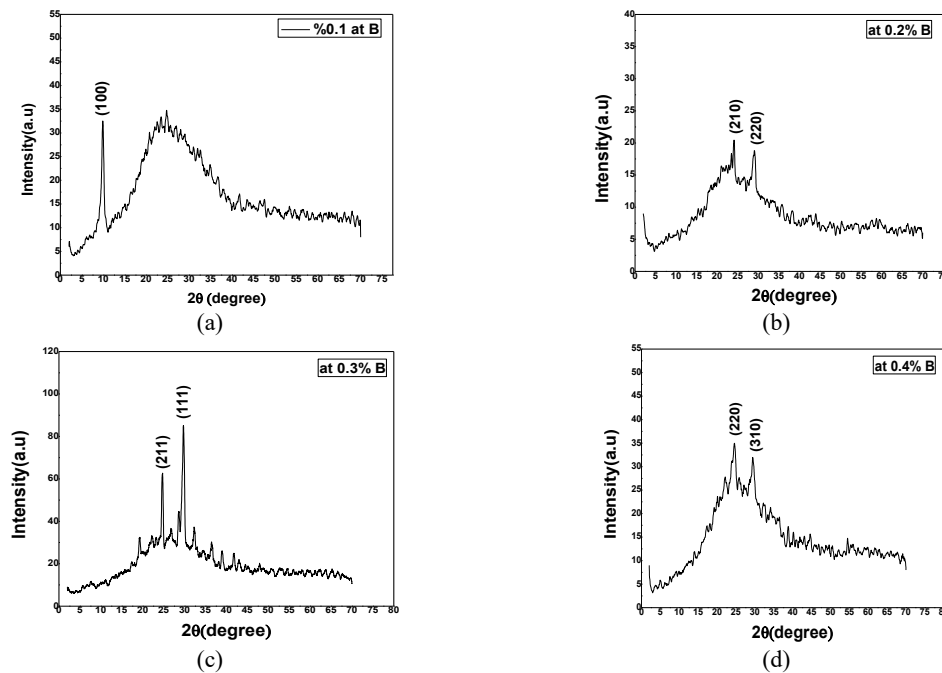


Figure 3. (a) B-doped ZnSe at 0.1 % Boron (b) B-doped ZnSe at 0.2 % Boron (c) B-doped ZnSe at 0.3 % Boron (d) B-doped ZnSe at 0.4 % Boron

The spectrum of pure ZnSe shows distinct diffraction peaks corresponding to the (211) and (220) planes around 24.11° and 29.25° in 2θ , consistent with the standard JCPDS pattern (No. 01-073-1764), confirming the crystalline nature of the sample. While bulk ZnSe with a cubic zinc blende structure typically exhibits dominant peaks at (111), (220), and (311) (D.V *et al.*, 2022), the prominence of the (211) and (220) reflections here suggests a preferred orientation or texture, likely influenced by the synthesis method. The relatively sharp but not extremely intense peaks, combined with the broad background, indicate that the material is nanocrystalline with partial amorphous content, a feature commonly observed in ZnSe thin films or chemically synthesised nanoparticles (Gupta *et al.*, 2025). Unlike doped or alloyed ZnSe, which often shows additional peaks or shifts due to lattice distortion, the absence of such features here confirms the phase purity of the sample (Mote *et al.*, 2013). Thus, the pattern reflects pure ZnSe with nanocrystalline characteristics and orientation effects, which aligns with observations in similar studies of non-bulk ZnSe systems (Emir *et al.*, 2025).

The XRD patterns of ZnSe doped with varying boron concentrations reveal that crystallinity strongly depends on the dopant level. At 0.1% B, the material shows a weak and broad (100) reflection, indicating poor crystallinity and a partial amorphous nature. With 0.2% B, crystallinity improves as the (210) and (220) phases emerge, showing enhanced lattice ordering. The highest crystalline quality is observed at 0.3% B, where sharp and intense reflection from the (211) and (111) planes appear, suggesting optimum dopant incorporation, larger crystalline size, and preferred orientation similar to bulk ZnSe. However, when the boron content increases to 0.4%, the peaks shift to (220) and (310), but broaden and lose intensity, indicating reduced crystallinity due to defect formation, lattice strain, and excess dopant incorporation. This behaviour is consistent with reports that moderate doping of VI semiconductors improves structural order, while excessive doping introduces structural distortion and decreases crystallinity (Hu & Zhang, 2006; Kumari *et al.*, 2025). Thus, 0.3% B represents the optimum concentration for enhancing ZnSe crystal growth, whereas higher concentrations destabilise the lattice.

The average crystalline size, estimated from the Debye-Scherrer equation, decreased slightly from 14.2 nm in undoped ZnSe to 13.9 nm at 0.4% B-doping. This subtle decrease is consistent with the XRD diagrams, where doping causes peak broadening due to lattice stress and structural disorder. At lower dopant levels, crystallinity improves and peaks sharpen, reaching optimum quality at 0.3% B. However, at 0.4% B, the peaks broaden again, indicating increased strain and a marginally smaller crystallite.

The incorporation mechanism of boron in the ZnSe lattice can be understood from its atomic size and bonding characteristics. Boron has a smaller covalent radius than both Zn and Se, making it capable of entering the ZnSe lattice either by substituting the Zn^{2+} ion or by occupying interstitial sites. At low doping levels, $\leq 0.3\%$, boron is likely to replace Zn atoms at cationic sites, forming B-Se bonds that locally compress the lattice due to the smaller ionic radius (Thakur *et al.*, 2022). This substitutional incorporation generates localised strain fields and modifies the charge balance by introducing shallow donor levels that can passivate native selenium vacancies. However, at higher concentrations, $>0.3\%$, the excess boron atoms cannot be accommodated at substitutional positions and tend to occupy interstitial sites, creating defect complexes or clusters that act as scattering or recombination centres (Hayami *et al.*, 2024). These interstitial boron species distort the

lattice further and may explain the observed peak broadening, reduced crystallinity, and increased resistivity at higher doping levels. Thus, the interplay between substitutional and interstitial incorporation governs the structural strain and electrical transport characteristics of B:Ze thin films.

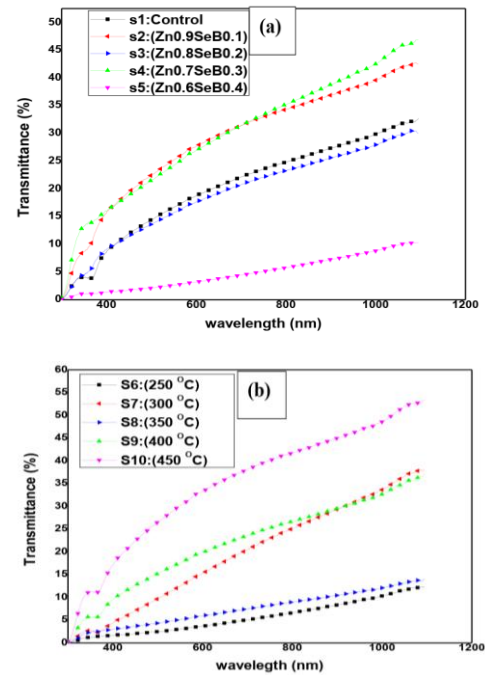


Figure 4. Graph of Transmittance against Wavelength (a) at variable boron concentration (b) at variable temperature of deposition

Optical Properties

Figure 4(a) presents the optical transmittance spectra of boron-doped ZnSe thin films with varying boron concentrations (S1 - S5). The transmittance increases systematically from the undoped film (S1) to the 0.3 mol boron-doped sample (S4), reaching a maximum value of about 45% in the visible region. This improvement is attributed to enhanced crystallinity and reduced defect-related absorption as boron atoms passivate selenium vacancies and improve film densification. However, at higher doping concentration (0.4 mol, S5), transmittance decreases sharply, indicating that excessive boron introduces lattice strain, defect clusters and possible secondary phase that promote light scattering and absorption. Figure 4(b) presents the optical transmittance spectra of boron-doped ZnSe thin films deposited at varying substrate temperatures. Transmittance increases systematically with temperature, indicating

progressive improvement in optical transparency with enhanced crystalline quality. Films deposited at 450°C exhibited the highest transparency (54%), while those grown at 250°C showed the lowest (12%). The rise in transmittance is attributed to reduced defect-related scattering and absorption as deposition temperature increases. As crystallinity improves at higher temperatures, light scattering diminishes, leading to enhanced transmittance, a trend consistent with earlier reports on solution-processed and thermally evaporated ZnSe films (Li *et al.*, 2023; Rahman *et al.*, 2025).

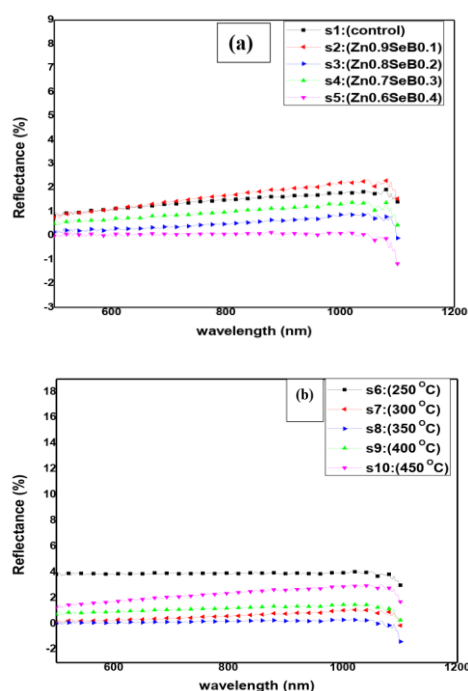


Figure 5. Graph of Reflectance against Wavelength (a) at variable boron concentration (b) at variable temperature of deposition

The reflectance spectra of the ZnSe: B and ZnSe deposited at varying boron doping and varying temperature are presented in Figure 5 (a and b). The film S2 has the highest reflectance (2%), followed by S1, S4, S3 and the lowest at S5. For films deposited at varying substrate temperatures presented, a clear dependence on growth temperature and boron doping is observed, with the film deposited at 250°C exhibiting the highest reflectance (approximately 4%), whereas films prepared at 300, 350, and 400°C showed significantly lower values of 1.7%, 0.1% and 1.9% respectively. At 450°C, reflectance increased slightly to 3%. Across all samples, reflectance values generally rose with increasing wavelength

from the UV to the near-infrared region, consistent with the intrinsic dispersion behavior of a wide-bandgap semiconductor (Tareque Chowdhury *et al.*, 2017). The exceptionally low reflectance of the 350°C film suggests minimised surface roughness and improved stoichiometric balance at this growth temperature, thereby reducing Fresnel losses and light scattering at the film-air interface. This trend aligns with previous studies on ZnSe and other II-VI chalcogenides, which reported that optimised growth conditions yielded low-reflectance surfaces suitable for optoelectronic integration (Rahman *et al.*, 2025).

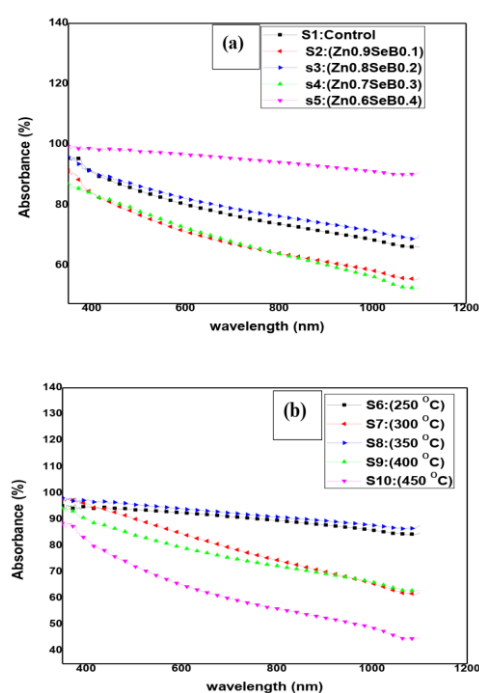


Figure 6. Graph of Absorbance against Wavelength (a) at variable boron concentration (b) at variable temperature of deposition

Figure 6(a) illustrates the optical absorbance spectra of ZnSe films with varying boron concentrations. All samples exhibit a gradual decrease in absorbance with increasing wavelength. The control sample, S1, shows the lowest absorbance, while absorbance progressively increases with higher boron incorporation, reaching a maximum for S5. This enhancement in absorbance can be attributed to the introduction of boron atoms, which create additional localized states within the band structure, thereby narrowing the bandgap and facilitating greater photon absorption. Consequently, boron doping improves the optical response of ZnSe films, making them

more suitable for optoelectronic applications. Figure 6(b) shows the influence of annealing temperature on the absorbance behaviour of ZnSe thin films. A similar decreasing trend in absorbance with wavelength is observed in all samples. However, the magnitude of absorbance strongly depends on the annealing temperature. S8 exhibits the highest absorbance, indicating improved crystallinity and reduced defect density, while higher annealing temperature (400) leads to a decline in absorbance, possibly due to grain coarsening or partial volatilization of selenium.

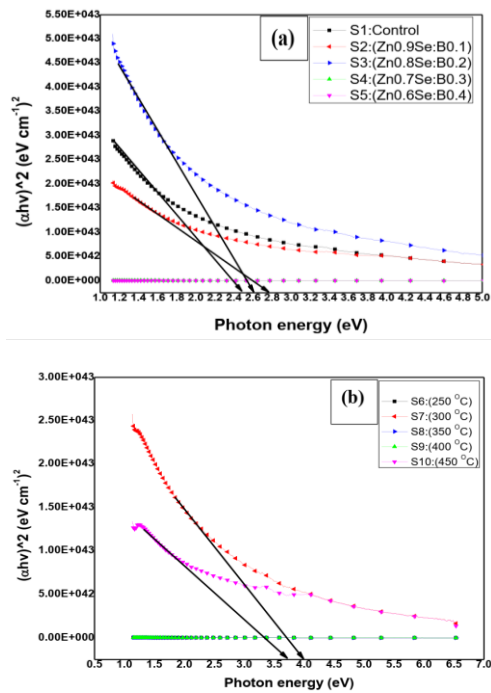


Figure 7. Tauc Plots of ZnSe Thin Film (a) at variable boron concentration (b) at variable temperature of deposition

Importantly, the optical bandgap energy obtained from the Tauc's plot is shown in Figure 7. The control sample, S1, exhibits the highest bandgap, whereas increasing boron concentration from S2 to S5 leads to a progressive shift of the absorption edge toward lower photon energies, indicating a decrease E_g (Figure 7a). This may be due to the introduction of defect states and band tailing (Emir *et al.*, 2025). Conversely, (Figure 7b) shows that the E_g initially increased with temperature up to 300°C as film crystallinity improves, then slightly decreased at higher temperatures ($\geq 350^\circ\text{C}$) because of structural defect caused by grain coalescence. These values are higher than those typically reported for CBD or the

thermal evaporation method, underscoring spray pyrolysis as a viable alternative for producing wide-bandgap ZnSe films (Tareque Chowdhury *et al.*, 2017).

Figure 8(a) and Figure (b) presents the optical density of the synthesised ZnSe films for the varying boron doping and varying temperature of deposition. Optical density increases linearly with thickness up to a certain point, until deviation due to scattering, inhomogeneity or surface effect (Zaka *et al.*, 2024). Both figures show a significant increase that later overlapped and deviated at 4×10^{-9} eV. S5 showed an increase in optical density from the control to 0.2 and 0.4 boron doping concentrations and a decrease in value from S2 at 0.1 and S4 at 0.3 boron doping. A drastic decrease with an increase in temperature of deposition was recorded; however, at 350°C, an increase was observed contrary to the other samples.

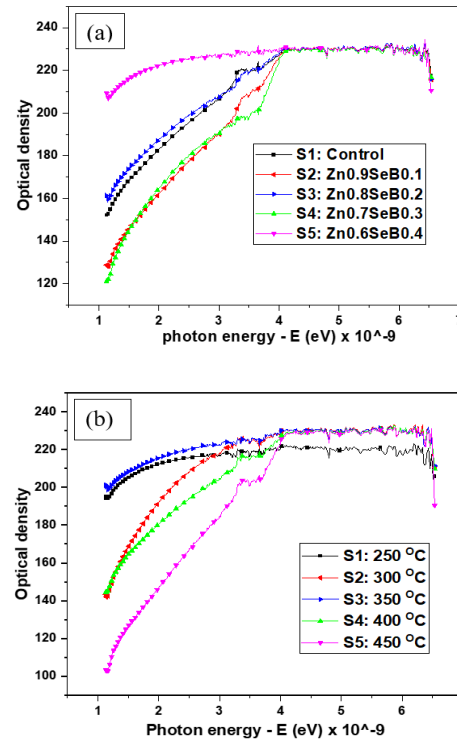


Figure 8. Graph of Optical Density against Photon Energy of the deposited ZnSe (a) at variable boron concentration (b) at variable temperature of deposition

Figure 9 shows the refractive index of the samples deposited at varying doping concentrations and temperature of deposition. Both figures show a zero-value refractive index which implies that the phase velocity of the light becomes extremely large

and the wavelength inside the material approaches infinity. This condition is called the epsilon-near-zero (ENZ) value of refractive index across the UV-VIS-NIR region. It enables ultrafast and efficient light modulation, which is valuable for optical switches and photonic devices (Caspani *et al.*, 2016).

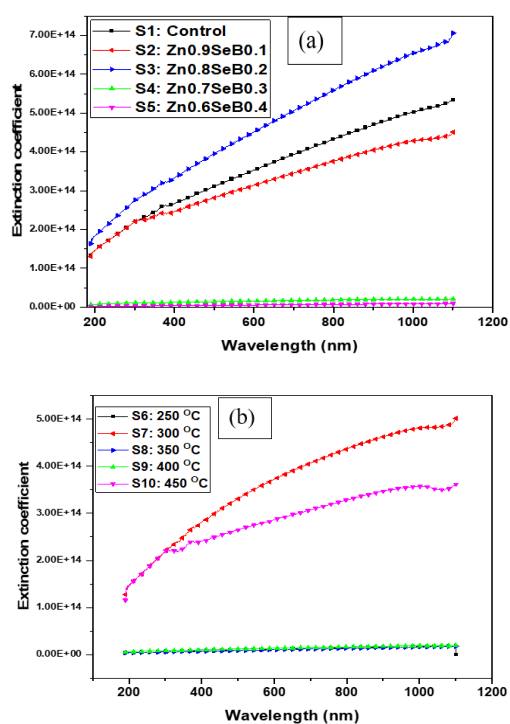


Figure 9. Graph of Extinction Coefficient against Wavelength of the deposited ZnSe (a) at variable boron concentration (b) at variable temperature of deposition

Figure 10(a and b) shows the variation of refractive index with wavelength for boron-doped ZnSe thin films and those deposited at different substrate temperatures. In both cases, the refractive index exhibits large fluctuations between 200 - 400 nm, and then remains nearly constant at zero beyond this range. These irregularities indicate possible measurement noise, computational errors, or improper data processing rather than material behaviour. Typically, ZnSe thin films exhibit a positive refractive index ranging from 2.4 to 2.8 in the visible region, as reported by Tareque Chowdhury *et al.* (2017)

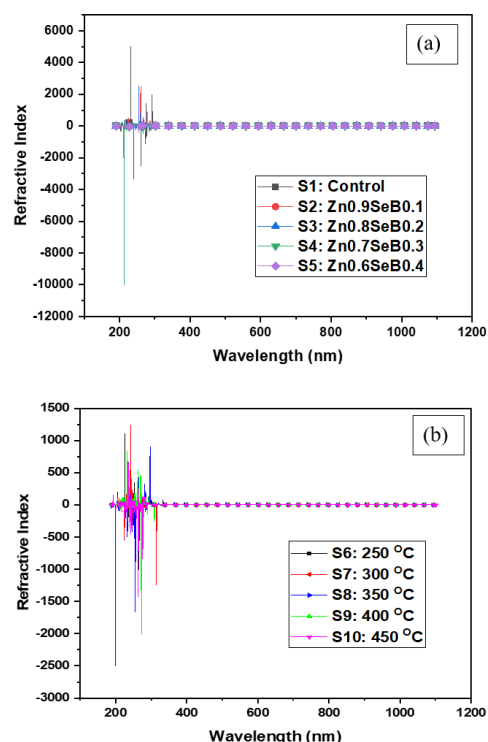


Figure 10. Graph of Refractive Index against Wavelength of the deposited ZnSe (a) at variable boron concentration (b) at variable temperature of deposition

Morphological Properties

Figure 11 shows the SEM micrographs of the pristine ZnSe and B: ZnSe samples. These micrographs were captured at magnifications of 5000X and 2500X, with an accelerating voltage of 16.0 kV and 17.2 kV respectively. The undoped ZnSe (a) sample exhibits a heterogeneous microstructure composed of discrete, non-agglomerated grains with irregular shapes and sharp edges. The morphology resembles a flower-like or petal-like aggregation, with the individual crystallites radiating outward, likely indicative of preferential crystal growth along specific crystallographic directions. Similar hierarchical structures have been reported in Zn-based chalcogenides, where such self-assembly is driven by minimisation of surface energy during crystal growth under controlled conditions (Shen *et al.*, 2010). This morphology is favourable for optoelectronic applications, as it can offer a high surface area-to-volume ratio and expose a greater

number of reactive sites, which can enhance photon absorption and exciton dissociation in photovoltaic or photocatalytic systems (Mohammadi *et al.*, 2025).

Upon boron doping, a marked alteration in surface texture and microstructure is observed. The B: ZnSe (b) composite exhibits a significantly more agglomerated and compact morphology with reduced interparticle spacing and an overall rougher texture. The particles appear to be fused or sintered together, likely due to enhanced nucleation and crystal growth processes triggered by boron incorporation. Such agglomeration could be attributed to the increased electrostatic interactions or enhanced van der Waals forces between adjacent

particles as a result of boron substitution within the ZnSe lattice. Boron doping may have introduced defect states or localised charge regions, which facilitate interparticle connectivity and create denser film structures. The observations here are consistent with previous results of B-doped II - VI semiconductors, where boron was found to induce morphological densification and promote grain coalescence (Chi T. Cao *et al.*, 2022).

Electrical Properties

The electrical characteristics of the ZnSe and B-doped thin films are summarised in Table 2 and Table 3.

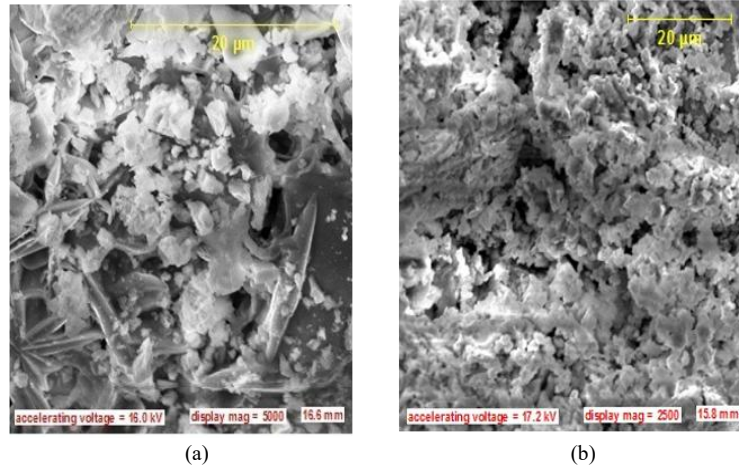


Figure 11. SEM analysis for (a) undoped ZnSe and (b) B-doped ZnSe thin films

Table 2. The Hall Effect Results of the ZnSe Thin Films at Variable Temperature of Deposition

T°C	(ρ) (Ωcm)	(n) (cm^{-3})	(μ) $\text{cm}^2(\text{VS})^{-1}$	t (μm)	(RH) cm^3C^{-1}
250	2.87×10^4	-2.89×10^{11}	7.55×10^2	0.950	-2.162×10^7
300	8.69×10^2	-3.70×10^{13}	1.94×10^2	0.025	-1.686×10^5
350	6.14×10^4	-2.46×10^{11}	4.13×10^2	1.000	-2.535×10^7
400	6.78×10^4	-2.64×10^{12}	3.49×10^1	0.650	-2.367×10^6
450	3.10×10^3	-9.39×10^{11}	2.15×10^3	0.025	-6.651×10^6

Table 3. Hall Effect parameters for B-doped ZnSe

Conc. of B	(ρ) (Ωcm)	(n) (cm^{-3})	(μ) $\text{cm}^2(\text{VS})^{-1}$	t (μm)	RH cm^3C^{-1}
0	1.12×10^3	-1.19×10^{12}	4.66×10^3	0.025	-5.231×10^6
0.1	1.73×10^3	-9.63×10^{11}	3.74×10^4	0.025	-6.483×10^6
0.2	4.32×10^3	-5.06×10^{12}	2.86×10^2	0.020	-1.235×10^6
0.3	1.97×10^3	-7.21×10^{12}	4.40×10^2	0.500	-8.655×10^5
0.4	3.03×10^4	-7.18×10^{10}	2.87×10^3	2.000	-8.692×10^7

For undoped ZnSe, resistivity decreased with increasing deposition temperature up to 450°C, consistent with improved crystallinity and the reduction of defect-mediated scattering at elevated growth conditions. The highest mobility was observed at 450°C ($2.15 \times 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), confirming that charge carrier transport benefits from reduced grain boundary density and enhanced film compactness at higher growth temperatures. Similar temperature-driven mobility enhancements have been reported in ZnSe and ZnO films grown by spray pyrolysis and related techniques (Mishra *et al.*, 2021). Incorporation of boron significantly modified the electrical transport. Undoped ZnSe exhibited a resistivity of $1.12 \times 10^3 \text{ } \Omega \cdot \text{cm}$ and mobility of $4.66 \times 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, values consistent with those of wide-bandgap II – VI semiconductors (Tareque Chowdhury *et al.*, 2017). At low doping (0.1% B), resistivity increased marginally to $1.73 \times 10^3 \text{ } \Omega \cdot \text{cm}$, but carrier mobility rose to $3.74 \times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, indicating that shallow boron incorporation initially passivated defects and reduced carrier trapping. At higher boron concentration, however, both resistivity and carrier scattering increased markedly, likely due to the formation of defect complexes and impurity states that act as recombination centres. Such trade-offs between carrier concentration and mobility under heavy doping are well documented in ZnO: B and ZnSe: Cu systems (Abdel-Salam *et al.*, 2023). The negative Hall coefficients observed across all samples confirm their n-type, which may originate from intrinsic selenium vacancies as well as boron-induced donor states. Interestingly, the extreme case of 0.4% B-doping showed a reduced carrier concentration ($7.18 \times 10^{10} \text{ cm}^{-3}$) but relatively high mobility ($2.87 \times 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), suggesting that boron at this concentration promotes long-range carrier transport by stabilising the extended lattice order despite reducing free carrier density. This non-linear doping-temperature interaction highlights the complexity of defect chemistry in ZnSe thin films and suggests a route for balancing conductivity and transparency, critical for applications in transparent conductive electrodes and window layers in heterojunction solar cells (Ji *et al.*, 2022).

Quantitative comparison of carrier concentration and mobility between undoped and doped films provides insight into boron's role in defect passivation. Introduction of boron into the ZnSe lattice likely replaces Se or occupies interstitial sites, introducing shallow donor sites that interact with native Se vacancies. Its interaction reduces the compensating defect density, thereby modulating the free-carrier concentration. The increase in Hall mobility at low boron content

(0.1 - 0.3%) indicates a decrease in ionised impurity scattering, consistent with reduced defect levels. Conversely, excessive boron incorporation (>0.3%) creates deep-level traps or B-B complexes that act as recombination centres, increasing resistivity and reducing carrier concentration. Thus, boron simultaneously alters both lattice strain and defect equilibria, leading to tunable electrical transport properties.

Correlation of Boron Concentration and Temperature Microstructure, Optical and Electrical Properties

With increasing substrate temperature, the films show improved crystallinity, lower defect scattering and smoother surfaces which reduce optical scattering, increase transmittance, and produce a systematic bandgap widening from 3.64 - 3.75 eV. Boron plays a secondary but important role. Low to moderate B doping improves order (optimum at 0.3%) by promoting nucleation and defect passivation, whereas higher B doping (0.4%) creates strain, peak broadening and defect complexes that degrade crystallinity. Electrically, temperature generally reduces resistivity and increases mobility, while boron causes a non-linear defect. Small boron concentration reduces trapping and improves mobility, but higher doping introduces impurity scattering and reduces concentration in some cases.

Linking Crystallinity, Defect Modification and Electrical Properties

The electronic behaviour of the ZnSe and boron-doped ZnSe thin films can be directly related to their structural and defect characteristics. Improved crystallinity at elevated substrate temperatures reduces grain boundary density and internal strain, thereby lowering scattering centres for charge carriers and enhancing carrier mobility. In poorly crystalline films, numerous grain boundary and microstrain regions act as potential barriers that trap or scatter carriers, leading to high resistivity. Boron incorporation modifies this microstructural-electronic relationship through defect engineering. At low doping levels ($\leq 0.3\%$), boron atoms preferentially substitute for Zn^{2+} sites, generating shallow donor levels that compensate native selenium vacancies and reduce defect-induced carrier trapping. This defect passivation enhances electronic conduction and improves mobility by facilitating more continuous carrier pathways across grains. However, at higher concentration (>0.3%), boron tends to occupy interstitial sites or form complexes, which introduce localised states within the bandgap. The combined

effect of temperature and boron concentration, therefore defines the balance between defect annihilation and defect creation.

Conclusions

In this study, the deposition and characterisation of ZnSe thin films have been successfully achieved through the spray pyrolysis technique from the aqueous solution of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, SeO_2 , and HNO_3 , using distilled water and isopropanol as solvents. The results obtained revealed that the energy band gap values of the thin films increased with the deposition. As the temperature of deposition and the film thickness changed, other optical properties such as transmittance, absorbance, and absorbance coefficient of the films were affected. Qualitative evaluation of strain and carrier modulation demonstrated that boron acts as a dual structural-electronic modifier in ZnSe thin films. The dopant not only introduces local compressive strain that influences crystallite evolution but also modifies native defect populations, thereby affecting carrier transport. These effects explain the observed non-linear variation of resistivity and mobility with boron concentration and underscore the tunability of ZnSe via light-element doping.

This provides a wide range of applications of the thin films in solar cell fabrication, screening off UV radiation that is harmful to human beings and animals due to its high absorbance, low transmittance, and low reflectance in the UV region, eyeglasses coating, solar thermal conversion, solar control, anti-reflection coating, and window layers in solar cells. The optical bandgap value of the deposited ZnSe thin film has been determined to be 3.7 eV, making it a suitable candidate for a window layer in photovoltaic applications. The characterisation of ZnSe thin film was not sufficiently studied in this study due to lack of sufficient funds. More characterisation techniques should be done where the properties of ZnSe thin films, such as EDS, FTIR, AFM, and FSEM, will be explored to know the bulk properties of the films.

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Author Contributions

Conceptualization: Q.A.A., K.O.R., R.B., W.A.A., J.A.R., M.A.S.; Methodology: Q.A.A., K.O.R., R.B., W.A.A., J.A.R., M.A.S., A.O.A.; Investigation: Q.A.A., K.O.R., R.B., W.A.A., J.A.R., M.A.S., A.O.A.; Data Curation: Q.A.A., W.A.A., M.A.S., D.O.A., S.O.A., K.K.B., A.D.A., T.T.A., R.O.O., O.F.A., T.O.F., M.M.D.; Writing – Original Draft: Q.A.A., W.A.A., M.A.S.; Writing – Review & Editing: Q.A.A., W.A.A., M.A.S., D.O.A., S.O.A., K.K.B., A.D.A., T.T.A., R.O.O., O.F.A., T.O.F., M.M.D.; Supervision: Q.A.A., K.O.R., R.B., J.A.R. All authors have read and agreed to the published version of the manuscript.

Ethics Statement

Ethical approval was not required for this study because it did not involve human participants, animals, identifiable personal data, or materials requiring institutional ethical review.

Declaration of Generative AI Use

The authors declare that no generative AI tools were used in the preparation of this manuscript.

Conflict of Interest

The authors declare no conflicts of interest related to this work.

Data Availability Statement

The datasets generated and/or analyzed during the current study are available from the corresponding author upon reasonable request.

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