



OPTICAL CHARACTERIZATION OF TIN SELENIDE (SNSE) THIN FILMS PREPARED BY THERMAL EVAPORATION FROM ELEMENTAL PRECURSORS (SE) AND (SN)

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ABSTRACT

Tin selenide (SnSe) thin films with a thickness of ($t = 166\text{nm}$) were prepared by direct thermal evaporation of a mixture of its elemental precursors, Selenium (Se) and Tin (Sn), in a 1:1 molar ratio on glass substrates at room temperature. X-ray diffraction (XRD) and morphological analysis (SEM/AFM) confirmed that the as-deposited sample possesses a pure orthorhombic crystalline phase, whereas stepwise thermal treatment led to phase decomposition and impurity formation. Optical analysis revealed a high absorption coefficient ($\alpha > 10^5\text{ cm}^{-1}$) and two bandgaps: a direct gap of 1.42 eV and an indirect gap of 0.65 eV. The experimental results demonstrate the viability of these films as efficient, low-cost active materials for solar cell and broadband photodetector applications.

KEYWORDS: Tin selenide, Thermal evaporation, Bandgap energy, Optical constants.

2. INTRODUCTION

Within the family of inorganic semiconductors, group (IV–VI) chalcogenides have attracted intense research interest due to their tunable bandgaps, high absorption coefficients exceeding 10^5 cm^{-1} , and remarkable chemical stability.^[1] In this context, tin selenide (SnSe) emerges as a highly promising material, crystallizing in the orthorhombic system (space group Pnma) with a distinctive layered structure characterized by closely packed atomic layers.^[2] This arrangement imparts exceptional optical properties, manifested in a direct bandgap typically ranging from 0.9 to 1.3 eV in the bulk state, which extends to a broader range of (1.2–1.8) eV in thin films.^[3] Notably, some scientific literature attributes the bandgap to direct electronic transitions,^[4,5] while others ascribe it to indirect transitions.^[2,6] Current literature suffers from reference dispersion resulting from inaccurate stoichiometric control, a lack of precise understanding of the low-temperature thermal stability limits of SnSe, and a deficiency in linking phase purity to optical response parameters ($\tilde{\epsilon}, \sigma_{opt}$). Therefore, this

work aims to bridge this gap by presenting a unified experimental framework that demonstrates avoiding excessive (destructive) thermal treatments is a fundamental prerequisite for achieving reliable optical properties.

3. Sample Preparation and Deposition Conditions

SnSe thin films were deposited via vacuum thermal evaporation (5×10^{-6} mbar) onto clean glass substrates maintained at room temperature. High-purity elemental Sn and Se powders (99.99%) were mixed in a precise 1:1 molar ratio and hydraulically pressed into cohesive pellets to prevent powder scattering during evaporation. The substrates were mounted on a rotating holder at a source-to-substrate distance of 12 cm to ensure thickness uniformity. The crucible temperature was gradually increased under controlled conditions to achieve stable evaporation, enabling the growth of a homogeneous film as summarized in Table (1), which lists the deposition parameters.

Table (1): Deposition parameters for tin selenide (SnSe) thin films.

Deposition Time (sec)	Thickness (nm)	Deposition Rate (nm/s)
83	166	2

4. RESULTS AND DISCUSSION

4.1. Structural Results

4.1.1. X-ray Diffraction (XRD) Pattern of the As-Deposited Sample.

Given the strong correlation between the optical properties and the microstructure of semiconductors, we initiated the structural characterization of the films

using X-ray diffraction (XRD) to identify the dominant phase and verify the completion of the reaction between the elemental precursors (Sn, Se).

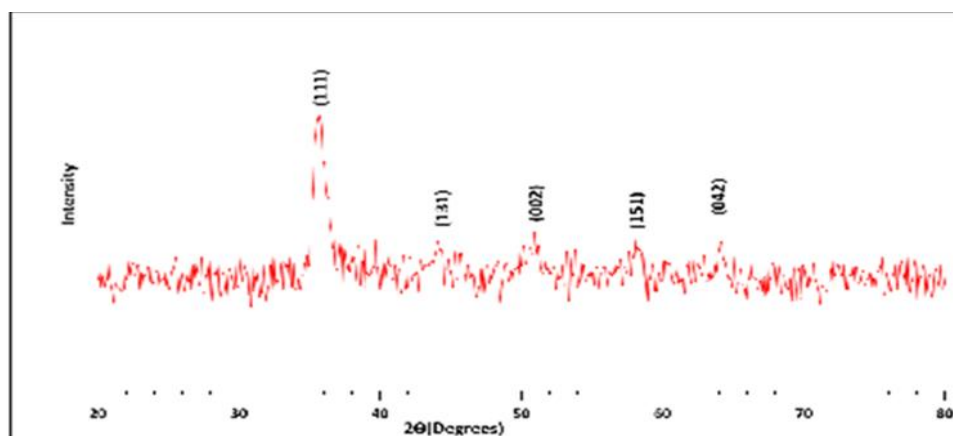


Figure (1): XRD Pattern of our Sample Prepared Before Thermal Annealing.

As shown in Figure (1), the sharp diffraction peaks at the crystallographic planes (111), (131), (002), (151), and (042) reveal an orthorhombic polycrystalline structure that matches perfectly with the reference card.^[4] (JCPDS Card No. 01-075-1843), which is a fundamental characteristic of group (IV-VI) compounds.^[2] The spectrum exhibits a strong preferred orientation along the (111) plane at a diffraction angle of $2\theta \approx 35.5^\circ$, attributed to the high atomic density of this plane and its stability in thermally evaporated films.^[7] The sharpness of these peaks reflects good crystallinity resulting from the appropriate kinetic energy of the deposited atoms and the high vacuum conditions (5×10^{-6} mbar), which allowed for regular crystal growth without substrate

heating. Furthermore, the complete absence of any peaks corresponding to SnSe_2 or tin oxides confirms the efficiency of direct deposition with a 1:1 ratio in preventing selenium loss and maintaining the purity of the stable α -SnSe (Pnma) phase. This provides a solid foundation for a sharp absorption edge and qualifies the films for precise optical characterization free from secondary phase interference.

4.1.2. Scanning Electron Microscopy (SEM) Analysis

To evaluate chemical purity and surface structure, the as-deposited sample was analyzed using an SEM-EDX system.

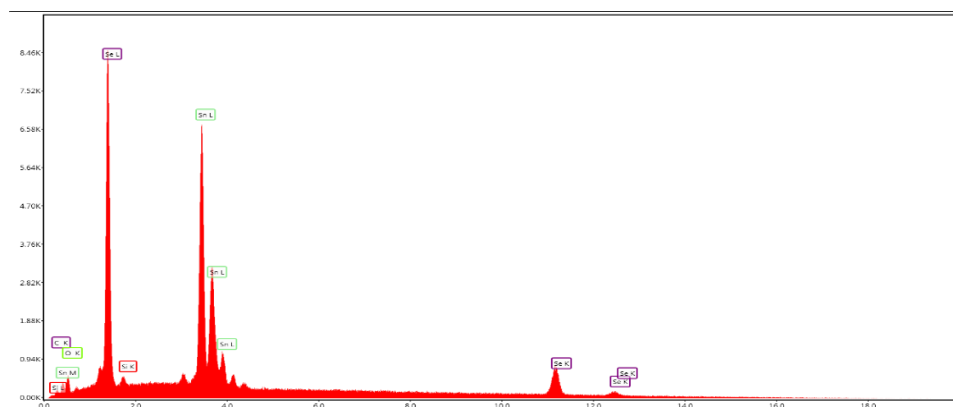


Figure (2): EDX analysis spectrum of our sample prepared before thermal annealing.

The EDX spectrum (Figure 2) displays distinct peaks for only Sn and Se elements, while the weak signals for Si,

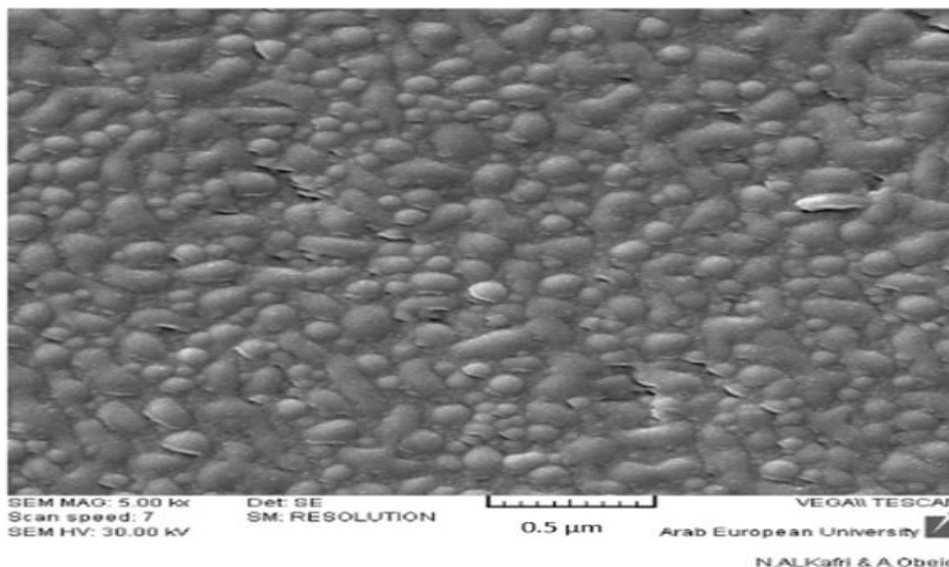
O, and C are attributed to the glass substrate.

Table (2): Weight and atomic percentages of the elements constituting the prepared sample.

Element	Atomic %	Weight %	Error %
Sn L	47.42	28.39	2.29
Se K	46.48	41.83	5.4
C K	2.82	16.69	15.21
O K	2.5	11.09	12.37
Si K	0.79	1.99	16.94

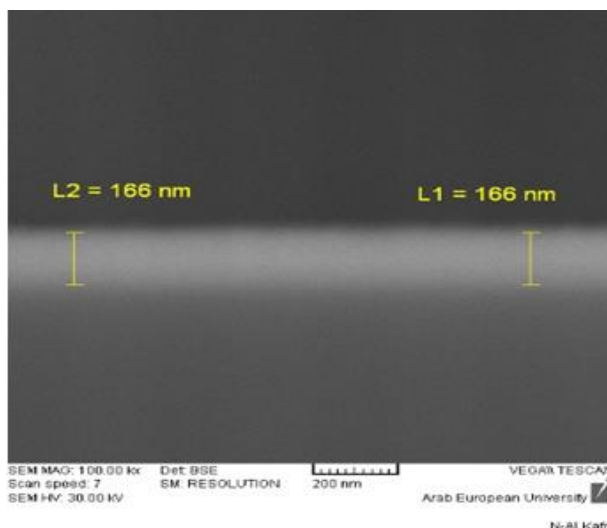
The quantitative results (Table 2) confirm that the atomic ratios of Sn (47.42%) and Se (46.48%) are very close to the ideal 1:1 stoichiometry, proving the compound's

purity and absence of secondary impurities due to the precision of the direct deposition method.

**Figure (3): 2D surface image of the sample.**

Microscopic examination (Figure 3) revealed a coherent surface with complete coverage and densely packed nanograins. This observation correlates directly with the sharpness of the XRD diffraction peaks, indicating good

crystallinity even at room temperature. To ensure the accuracy of optical calculations, the film thickness was measured via cross-sectional analysis (Figure 4).image.

**Figure (4): Cross-sectional.**

The average thickness was found to be 166 nm. This thickness is considered ideal for photovoltaic applications, as it provides a precise balance between

achieving a high absorption coefficient and minimizing internal stresses and costs compared to thicker films.

4.1.3. Effect of Stepwise Thermal Annealing on Phase Stability

The films were subjected to stepwise thermal annealing (50–200) °C for 30 minutes at each stage in an air atmosphere to evaluate their stability limits. XRD results (Figure 5) showed that the as-deposited sample maintains the purity of the α -SnSe (Pnma) phase, whereas the thermal treatment revealed high structural sensitivity manifested in two stages: First, in the range of (50–150)°C, a new peak appeared at $2\theta \approx 27.45^\circ$ corresponding to hexagonal SnSe_2 .^[8] accompanied by a decrease in the intensity of the main SnSe peak (35.5°). This partial decomposition is attributed to the weak van der Waals bonds between layers, which facilitate selenium sublimation and loss even at low temperatures.

Second, at 200°C, the SnSe_2 peak intensified, and a pattern indicating a cubic structure emerged; this is resulting from multi-phase interference rather than a stable phase transition, which requires temperatures >450°C.^[5] Consequently, the original as-deposited sample is considered the optimal choice for maintaining the pure orthorhombic structure and superior optoelectronic properties, given the deterioration of stoichiometric purity and impurity formation upon any subsequent thermal treatment in air.

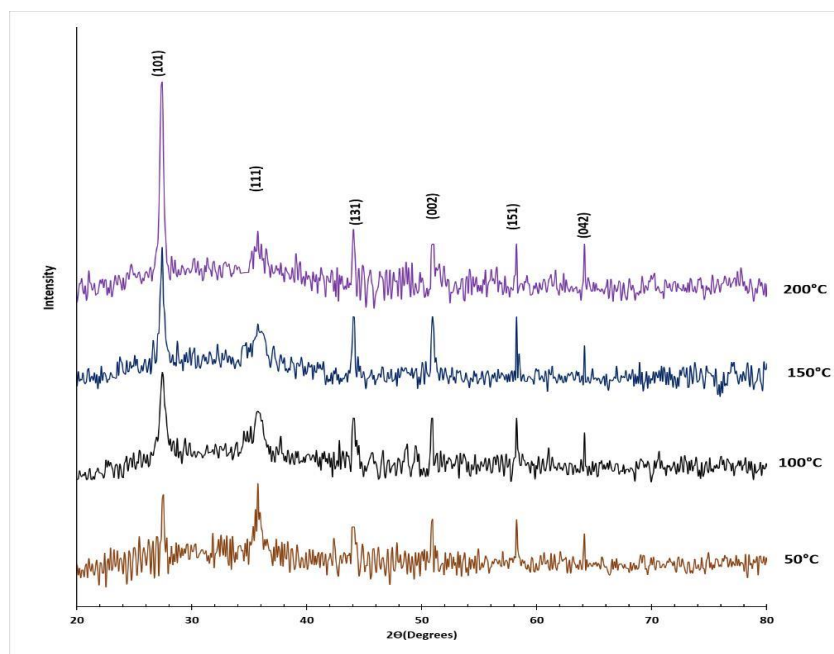


Figure (5): Crystallization stages undergone by SnSe films.

4.1.4. Topographical Characterization by Atomic Force Microscopy (AFM)

Given the phase stability of the as-deposited sample, AFM analysis was focused on this optimal state.

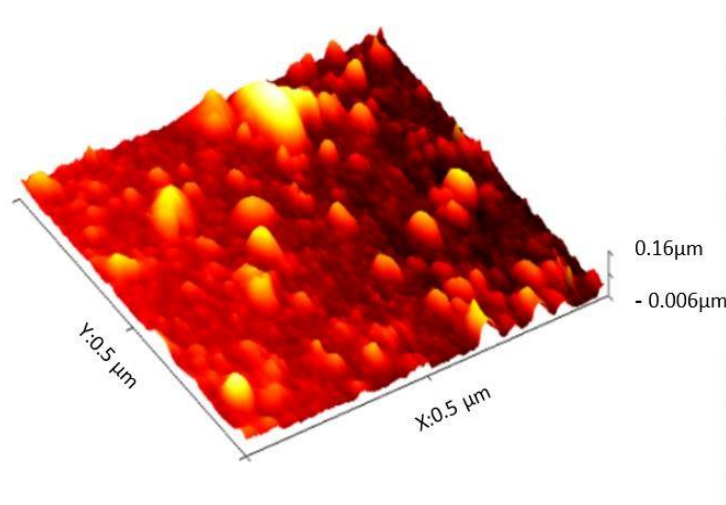


Figure (6): AFM image of the as-deposited sample.

The image (Figure 6) reveals a coherent and homogeneous surface characterized by densely packed nanograins free of cracks. This morphology correlates directly with the crystalline regularity and the preferred (111) growth orientation derived from XRD analysis. This structural-morphological homogeneity forms a crucial physical basis for the distinguished optical properties; specifically, surface smoothness and grain cohesion reduce light scattering at grain boundaries, enhance radiation penetration, and facilitate charge carrier transport. These features qualify the film as a highly efficient active layer for photovoltaic and photodetector applications.

4.2. Optical Results

4.2.1. Optical Transmittance and Reflectance Measurements of the As-Deposited Sample

The optical transmittance and reflectance of the thin film in its optimal state were measured across the spectral range of (320–2200) nm.

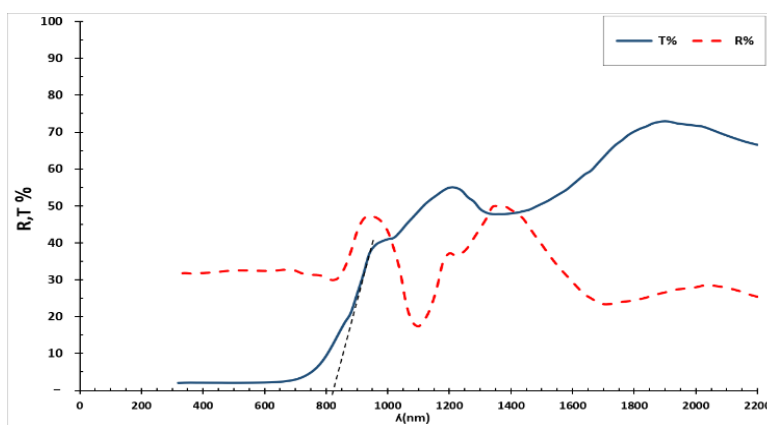


Figure (7): Transmittance (T) and reflectance (R) spectra of the thin film.

Figure (7) displays the transmittance (T) and reflectance (R) spectra of the as-deposited sample. A sharp decrease in transmittance is observed towards shorter wavelengths (nm), reflecting a distinct fundamental absorption edge indicative of direct electronic transitions, with an initial bandgap indicator at $\lambda \approx 825\text{ nm}$ ($E \approx 1.5\text{ eV}$), which aligns with recent literature on thermally evaporated SnSe films.^[4,7] In the near-infrared region (900–2200) nm, the transmittance exhibits high and stable values (55–80%) accompanied by regular interference fringes.

This serves as direct optical evidence of thickness uniformity and surface smoothness, confirming the SEM/AFM characterization results. Furthermore, the low reflectance values (10–40) % indicate a moderate refractive index, which contributes to minimizing optical losses and enhancing effective absorption, thereby supporting the viability of these films as active layers in photovoltaic and photodetector applications.

4.2.2. Calculation of the Absorption Coefficient

The absorption coefficient was calculated using Equation (1)^[9]

$$\alpha_{abs}(\omega) = \frac{1}{t} \ln\left(\frac{1-R}{T}\right) \quad (1)$$

where t is the film thickness.

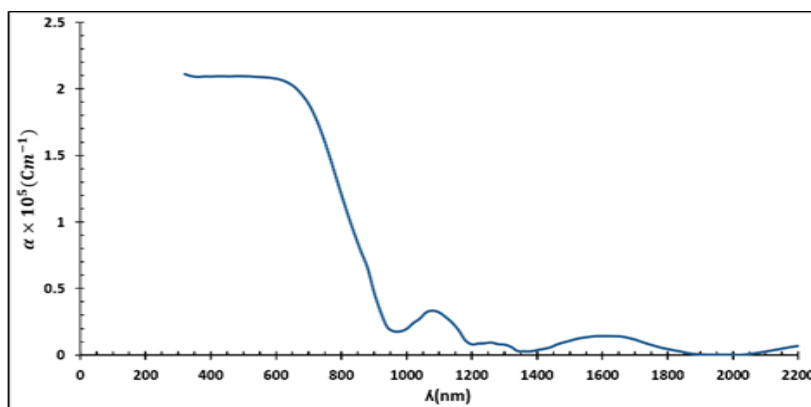


Figure (8): Absorption coefficient of the thin film.

Figure (8) shows the typical behavior of a semiconductor absorption coefficient, characterized by three main spectral regions that reflect the film's purity and electronic transitions: First, a weak absorption region ($\alpha \approx 0.3 \times 10^5 \text{ cm}^{-1}$) in the range of (900–1200) nm, attributed to indirect transitions, supported by the sample's purity from impurities as confirmed by EDX analysis. Second, a moderate absorption region ($\alpha \approx 1.1 \times 10^5 \text{ cm}^{-1}$) in the range of (820–900) nm, indicating the onset of dominant direct transitions at the absorption edge ($\lambda \approx 825 \text{ nm}$). Third, an absorption peak ($\alpha \approx 2.1 \times 10^5 \text{ cm}^{-1}$) in the visible and ultraviolet regions, confirming the material's efficiency as an effective absorbing layer. In the far-infrared region, the spectral tail stabilizes at low values

$$k(\omega) = \frac{c\alpha_{abs}(\omega)}{2\omega} \quad \text{or} \quad k(\lambda) = \frac{\lambda\alpha_{abs}(\lambda)}{4\pi} \quad (1)$$

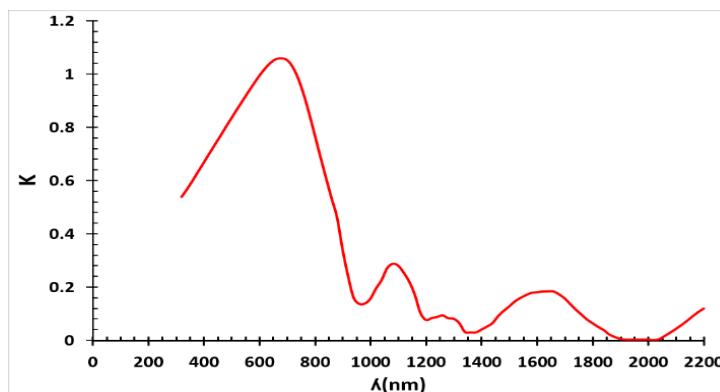


Figure (9): The extinction coefficient (k) for the SnSe thin film.

The spectrum of k (Figure 9) corresponds perfectly with the behavior of α , reaching a peak value of $k \approx 1.05$ at $\lambda \sim 700 \text{ nm}$, reflecting high absorption efficiency.^[2,4] In the infrared region ($\lambda > 1800 \text{ nm}$), the decrease of k towards zero confirms the purity of the Pnma phase and the absence of impurities, while the regular oscillations reflect thickness uniformity, consistent with the SEM/AFM results.

4.2.4. Calculation of the Refractive Index $n(\lambda)$:

The refractive index $n(\lambda)$ was calculated based on the relationship between the real and imaginary parts of the

$$\varepsilon_1(\omega_0) - 1 = \frac{2}{\pi} \int_0^\infty \frac{\omega \varepsilon_2(\omega)}{\omega^2 - \omega_0^2} d\omega \quad (3)$$

where (ω_0) is the natural frequency of the oscillator corresponding to the absorption peak. Using the physical relations ($\varepsilon_1 = n^2 - k^2$) and ($\varepsilon_2 = 2nk$) a direct

($\alpha \approx 0.1 \times 10^5 \text{ cm}^{-1}$), reflecting high transparency and excellent transmittance.^[3] These results are consistent with the highest published standards for thermally evaporated SnSe films.^[6]

4.2.3. Calculation of the Extinction Coefficient $k(\omega)$:

The extinction coefficient (k), which represents the imaginary part of the complex refractive index ($\tilde{n} = n + ik$), quantifies the material's ability to dissipate optical energy. It was calculated based on the absorption coefficient $\alpha(\lambda)$ using Equation (2).^[1]

complex dielectric function ($\tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2$), employing the Kramers-Kronig methodology. The real part of the dielectric function is expressed by the integral relation.^[10]

relationship, linking n to the extinction coefficient k can be derived.^[10]

$$n(\omega_0) - 1 = \frac{2}{\pi} \int_0^\infty \frac{\omega \cdot k(\omega)}{\omega^2 - \omega_0^2} d\omega \quad (4)$$

To adapt the calculation to experimental data measured in terms of wavelength, and by converting the integral using the relationship between k and α , we arrive at the

final practical formula for calculating the refractive index:

$$n(\lambda_0) - 1 = \frac{1}{2\pi^2} \int_0^\infty \frac{\alpha(\lambda)}{1 - \frac{\lambda^2}{\lambda_0^2}} d\lambda \quad (5)$$

where (λ_0) is the wavelength corresponding to the absorption peak. This methodology is consistent with

reference.^[11] and Figure (10) displays the calculated refractive index spectrum for the film.

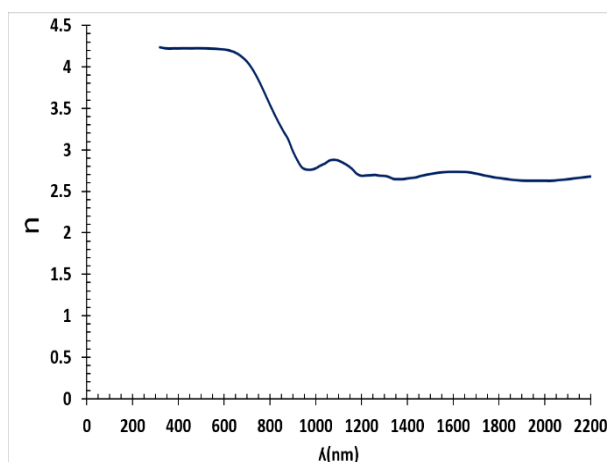


Figure (10): Refractive index spectrum $n(\lambda)$ for the as-deposited SnSe film.

Figure (10) shows the typical optical behavior of the refractive index n , with values ranging between 2.7 and 4.3, consistent with literature on orthorhombic SnSe films calculated by other methods.^[2,4] The curve exhibits normal dispersion (increasing n with decreasing λ), reaching a maximum of $n_{max} \approx 4.3$ at $\lambda \approx 700$ nm (just before the absorption edge). This reflects the high density of available electron states and aligns with the peak of the extinction coefficient k . In the infrared region ($\lambda > 1000$ nm), the value stabilizes at $n \approx 2.7$, confirming phase purity and the absence of absorbing impurities such as.^[8] This stability in the NIR range, coupled with high values in the visible region, makes the films optically compatible with glass and silicon substrates, positioning them as ideal candidates for anti-

reflection coatings and integrated photonic circuits, while preserving the material's intrinsic properties without distortion from thermal annealing.

4.2.5. Real and Imaginary Parts of the Complex Dielectric Function $\tilde{\epsilon}(\omega)$:

The complex dielectric function ($\tilde{\epsilon} = \epsilon_1 + i\epsilon_2$) was derived directly from the spectra of $n(\lambda)$ and $k(\lambda)$ using the fundamental relations: $\epsilon_1(\lambda) = n^2(\lambda) - k^2(\lambda)$ and $\epsilon_2(\lambda) = 2n(\lambda) \cdot k(\lambda)$. Figure (11) presents the calculated results.

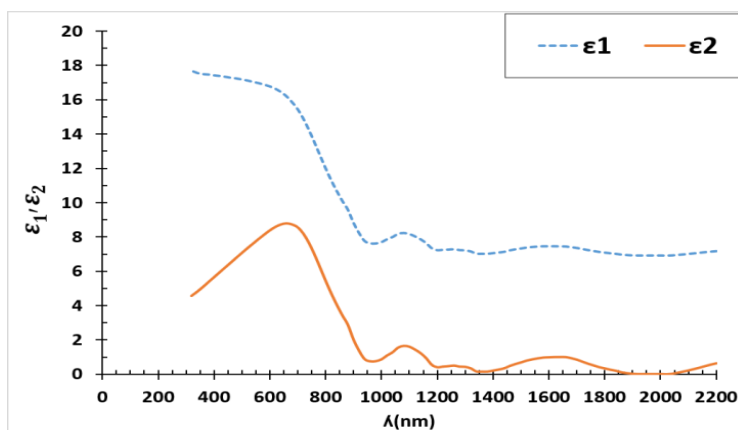


Figure (11): Spectra of the real part ϵ_1 and imaginary part ϵ_2 of the dielectric function for the SnSe film.

The real part ϵ_1 describes the stored energy (polarizability), reaching a peak value of 17.5 at the short wavelengths (350 nm) before stabilizing around 7.5 in the infrared region (>900 nm), reflecting the material's transitions.

The behavior of ϵ_2 can be interpreted based on quantum mechanical principles, where it is directly proportional to the absorption coefficient α_{abs} ^[10]

transparency. The imaginary part ϵ_2 , which

$$\epsilon_2(\omega) = \frac{nc}{\omega} \alpha(\omega) \quad (6)$$

Based on direct transition rules, α is related to the joint density of states and the probability of electron

transitions from the valence band (v) to the conduction band (c).^[10]

$$\alpha_{abs}(\omega) \sim \rho_{cv}(\hbar\omega) \sim \frac{m_0 E_g}{2} \cdot \frac{m_0}{m^*} \quad (7)$$

where ρ_{cv} is the joint density of states, and m_r is the reduced mass. Consequently, ϵ_2 takes the following form.^[10]

$$\epsilon_2(\omega) = \left(\frac{8\pi^2 e^2 \hbar}{m\omega} \right) f_{cv} \rho_{cv}(\hbar\omega) \quad (8)$$

where f_{cv} is the oscillator strength (representing the number of electrons participating in the oscillation). Thus, the decisive factor influencing both α and ϵ_2 is

the joint density of states, given by the surface integral.^[10]

$$\rho_{cv}(\hbar\omega) = \frac{2}{8\pi^3} \int_s \frac{ds}{\nabla_k(E_c - E_v)|_{E_c - E_v = \hbar\omega}} \quad (9)$$

The denominator represents the gradient of the energy difference between the valence and conduction bands. Physically, the flatness of the energy surfaces leads to a very small gradient in the denominator of Equation (9), causing a significant increase in ρ_{cv} and a maximum

value for ϵ_2 at a specific photon energy (critical point). This corresponds perfectly with the theoretical electronic structure of SnSe (Pnma) shown in Figure (12).^[2]

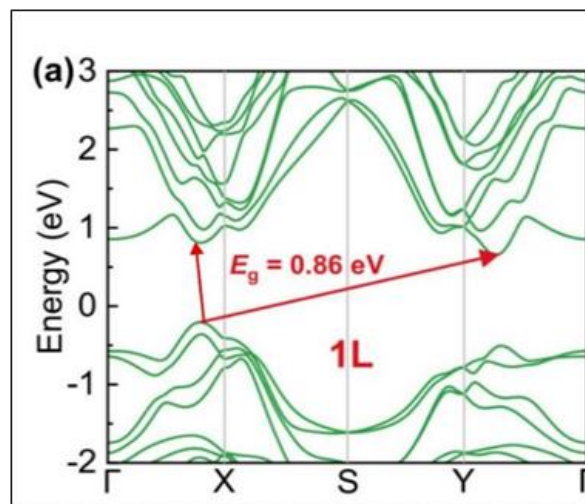


Figure (12): Theoretical energy band diagram of SnSe.

The observed peak in ϵ_2 indicates a superposition of multiple transitions at critical points (Γ, X, Y) with low gradients, while ϵ_2 decreases in the infrared region due to the divergence of energy surfaces and increased gradient.

It is worth noting that reference.^[2] focused on the indirect bandgap (0.86 eV), whereas the theoretical diagram also indicates direct transitions (~ 1.2 eV), which are close to our experimental value.

4.2.4. Optical Conductivity of As-Deposited Tin Selenide Thin Films

The optical conductivity $\sigma(\omega)$ serves as a quantitative measure of charge carrier response and energy

dissipation within the medium. It is directly related to the imaginary part of the dielectric function ϵ_2 through the following relation.^[12]

$$\sigma(\omega) = \frac{\omega}{4\pi} \epsilon_2(\omega) \quad (10)$$

By substituting ϵ_2 in terms of the absorption coefficient α , we obtain a linear relationship linking conductivity to absorption:

$$\sigma(\omega) = \frac{nc}{4\pi} \alpha(\omega) \quad (11)$$

Referring to the preceding quantum mechanical analysis, this relation indicates that $\sigma(\omega)$ is directly proportional

to the joint density of states ρ_{cv} and the probability of electronic transitions.

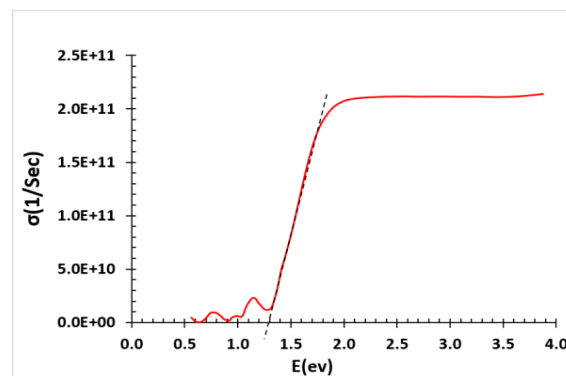


Figure (14): Optical conductivity spectrum $\sigma(\omega)$ of the SnSe thin film.

Figure (14) displays the $\sigma(\omega)$ spectrum for the as-deposited sample. The values approach zero in the far-infrared region ($E < 0.6$ eV), reflecting high transparency. However, a weak signal emerges at $E \approx 0.65$ eV, consistent with the indirect bandgap and specific critical points.^[7] In the visible region, the onset of direct transitions begins at $\hbar\omega \approx 1.1$ eV, with the transition probability density increasing significantly at eV. This confirms the material's high efficiency in converting optical energy within this spectral range.

4.2.5. Band Gap Energy (E_g)

To determine the band gap energy accurately, we employed the generalized Tauc relation, which links the absorption coefficient α to the incident photon energy $h\nu$, as given by Equation (12):

$$(\alpha h\nu) = B(h\nu - E_g)^m \quad (12)$$

where B is a constant dependent on the material properties, and E_g is the band gap energy. The exponent m indicates the nature of the electronic transitions, taking the value $m = 1/2$ for allowed direct transitions and $m = 2$ for indirect transitions. The value of E_g was determined graphically by extrapolating the linear portion of the $(\alpha h\nu)^{1/m}$ versus $h\nu$ plots to intersect the

energy axis, as shown in Figure (15). The values extracted in this work ($E_g^{dir} = 1.44$ eV and $E_g^{ind} = 0.65$ eV) are consistent with recent literature (Table 3). Although many previous studies have focused on the direct bandgap (~ 1.5 – 1.7 eV).^[4,5,7] our use of the generalized relation allowed for the precise identification of a low indirect bandgap (0.65 eV), which aligns with theoretical calculations for thin films.^[2] The slight decrease in the direct bandgap compared to some reference values is attributed to lattice strain effects and the thin-film nature (166 nm) of the sample prepared without annealing.^[4,5] These dual bandgaps reflect the complex electronic nature of the Pnma phase; while the direct bandgap ensures high absorption in the visible region, the indirect bandgap extends the spectral response towards the near-infrared, making these films ideal candidates for broadband absorption applications.^[2,6]

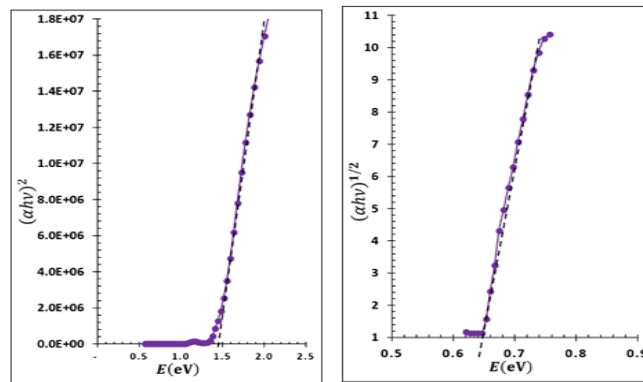


Figure (15a): The band gap for Direct transitions and figure (15b): the band gap for Direct transitions.

Table 3: Comparison of the bandgap energy (E_g) values for SnSe films with previous scientific studies.

References	Direct transitions	References	Indirect transitions
This work	1.44	This work	0.65
[3]	1.34 – 1.56	[13]	0.643
[4, [5] , [7]	1.5 – 1.7	[6]	0.9-1
[1]	1.4 – 1.5	[2]	0.9

5. CONCLUSION

This study concludes that direct thermal evaporation of elemental precursors (Sn, Se) with a controlled 1:1 molar ratio represents an effective and economical methodology for preparing high-purity SnSe thin films with a stable orthorhombic (Pnma) structure at room temperature. Structural analysis (XRD, SEM, EDX, AFM) demonstrated that any subsequent thermal treatment in an air atmosphere, even at low temperatures $\geq 50^\circ\text{C}$, inevitably leads to phase decomposition and the formation of SnSe_2 impurities. Consequently, the as-deposited state is optimal for preserving the material's intrinsic properties. Optically, the films exhibited a high absorption coefficient exceeding 10^5 cm^{-1} in the visible region and typical refractive index behavior ($n \approx 2.7 - 4.3$). Advanced analysis using the generalized Tauc relation and complex dielectric function revealed a distinctive dual electronic transition nature, manifested in a dominant direct bandgap of 1.44 eV and a lower indirect bandgap of 0.65 eV. This dual spectrum, supported by optical conductivity (σ_{opt}) and joint density of states calculations, extends the material's spectral response into the near-infrared region. The consistency of these properties with the bandgaps of traditional CdTe and Ge compounds, coupled with non-toxicity and raw material abundance, positions SnSe films prepared via this methodology as promising and sustainable candidates for next-generation multi-junction solar cells and spectral-selective photodetectors.

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