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# The impact of annealing on the optoelectronic properties of tin selenide thin films for photovoltaics

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In this study, Tin selenide (SnSe) was prepared via thermal evaporation from tin ingots and selenium powder followed by annealing at 250°C in an inert atmosphere of Argon gas. Two samples were used for characterization purposes, as-deposited and annealed. The structural parameters including particle size, strain, dislocation density, and number of crystallites per unit area were calculated from XRD while the optical properties including band gap were extracted from UV-visible spectroscopy. Four probe techniques were used to measure the electrical properties.

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*Keywords:* SnSe thin films, Solar cells, XRD, SEM, Spectroscopy

## 1. Introduction

The demand of electrical energy is increasing dramatically due to world population. The present sources of energy are not sufficient to provide the needs of the world and therefore the researchers are developing new energy technologies. The renewable energy resources have potential to face the future population challenges. There are many renewable energy technologies and among them solar energy has received much attention due to its free ingredients and steady output. Solar energy is a natural source of energy and is available freely to the whole world. It is an evergreen source of energy and requires suitable devices for conversion and storage for the benefit of human beings. Photovoltaics has paved the way for the conversion of energy while the battery is used for the storage process [1]. In photovoltaics, the Solar cell is a particular device that is used consistently for its conversion into electrical energy. There are many solar cells already commercialized and have been used for conversion purposes. However, their efficiency and other parameters are not suitable to meet the current world requirements. It is therefore suggested to reduce the cost of solar cells and increase the output parameters. The use of silicon, cadmium telluride, zinc telluride, etc. are already commercialized solar cells, and their output parameters are stuck to one point as no increase in their efficiency was observed in the last few years. The researchers are now working on new materials as an absorber layer to be used as an alternative to silicon and other thin film materials. Tin selenide (SnSe) is one such material whose properties as an absorber layer have not been studied extensively yet [2].

Tin selenide (SnSe) is a binary compound composed of tin (Sn) and selenium (Se). It is a crystalline material that belongs to the group IV-VI semiconductors, also known as chalcogenides. Tin selenide has gained significant attention in recent years due to its unique electronic, thermal, and optical properties, which make it a promising material for various applications. One of the notable properties of tin selenide is its excellent thermoelectric performance. It exhibits a high thermoelectric figure of merit (ZT), which is a measure of a material's efficiency in converting

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waste heat into electricity [3-5]. This makes tin selenide suitable for thermoelectric applications, such as waste heat recovery in power generation, automotive waste heat recovery, and other energy harvesting devices. Tin selenide also exhibits interesting electronic properties, including a narrow bandgap and high carrier mobility, which make it potentially suitable for optoelectronic applications such as photovoltaics, photodetectors, and optoelectronic switches. Additionally, tin selenide has been studied for its potential in other applications, such as phase change memory, as a catalyst for chemical reactions, and as a component in thin-film transistors. Tin selenide can be synthesized through various methods, including physical vapor deposition (PVD), chemical vapor deposition (CVD), and solution-based methods. Its properties can be tuned by adjusting the synthesis conditions and doping with other elements to modify its electronic and thermal properties [6].

SnSe is cheap, non-toxic, and highly abundant material. The high absorption coefficient and high yield for charge carriers with large diffusion length and small recombination length make it very impressive for photovoltaics. Tin selenide belongs to the binary compound family of group IV-VI [7]. Physical properties of SnSe deposited via atomic layer deposited (ALD) thin films were first reported by Drozd et al.in 2009 [8]. They used different substrates for the deposition of SnSe thin films such as mica, silicon, and quartz within the temperature range of 200-400°C. Thin film deposition was carried out at a substrate temperature of 300°C and showed sphere-shaped grain having a low band gap ($E_g$=1.15 eV). Shengiae et al. [9] reported the synthesis of tin selenide by electrochemical atomic layer deposition with high open circuit voltage and short circuit current. Mott–Schottky studies showed that tin selenide is a p-type semiconductor with a band gap of 1.25 eV. Terada reported a two-step evaporation method for tin selenium alloy [10]. He also showed that the evaporation method is superior in controlling SnSe thin film thickness and impurity contents of the deposited film. Bennouna and Tran prepared a thin film of tin selenide at 350A°/min deposition rate and reported its optoelectronic and structural properties. The electronic state density of states was also reported by Reddy et al. [11] with UV electron spectroscopy which resulted in an electron affinity and first threshold of 4.70 eV and 5.60 eV respectively. It has been noticed that the resistivity of as-deposited thin films decreases with the increase in annealing temperature, whereas an increase in the Hall mobility and carrier density was also observed. The 250 nm thin film deposited at room temperature showed the carrier concentration, resistivity, Hall mobility, and band gap as $4.40\times10^{17}$ $cm^{-3}$, 33.0 Ω-cm, 8.90 $cm^2$ $V^{-1}$ $s^{-1}$, and 1.21 eV, respectively [12]. The properties of tin selenide are rapidly changing by changing substrate nature and source temperature so large numbers of study is available on thin film growth and characteristic by changing thickness and temperature. Despite its promising properties, tin selenide also faces challenges in terms of stability, scalability of synthesis, and device integration. Further research and development efforts are ongoing to fully understand and optimize the properties of tin selenide for various applications, and to address these challenges to enable its practical use in commercial applications. In the current study, thin films of SnSe will be studied and the effect of annealing temperature will be comprehended.

## 2. Experimental

It's important to note that this is a general synthesis method, and specific details may vary depending on the intended application or research requirements. The thermal evaporation method is utilized for the deposition of tin selenide thin films. The thermal evaporation technique is a physical vapor deposition (PVD) technique that is used to deposit a target material on a commercial glass substrate. The benefit of this method is that the evaporation is performed in a high vacuum environment at a pressure of $10^{-4}$ torr as the substrate is less contaminated and the thin film prepared is in pure form. The heat energy is transferred to the source material and is vaporized and deposited on the substrate after condensation. [12]. The source material is placed in a molybdenum boat and it is heated by a current source rated 15A. Two source techniques were utilized for the fabrication of the thin films and the starting materials were tin granules and selenium powder. The distance between the substrate to source was kept at 15 cm. The thickness

of the film is about 500 nm measured by a quartz crystal monitor. After deposition, the thin film was annealed (heat treatment) in an inert atmosphere for one hour.

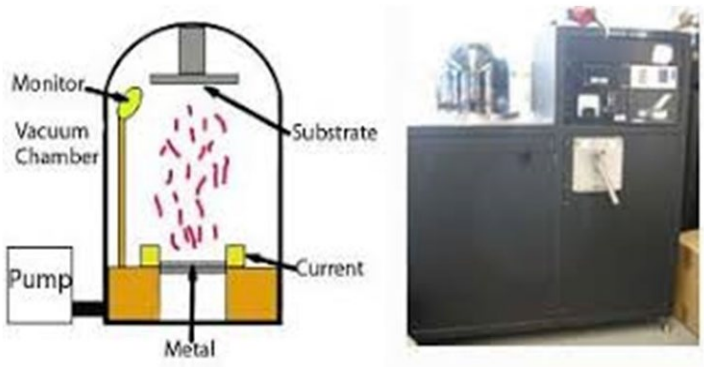


*Fig. 1. Schematic diagram for thermal evaporation technique.*

## 3. Results

The structural analysis of tin selenide (SnSe) involves the determination of its crystal structure, which provides important information about its arrangement of atoms and bonding. The most stable phase of SnSe is the orthorhombic structure, which exhibits an anisotropic layered structure. X-ray Diffraction (XRD) is a widely used technique to determine the crystal structure of materials. It involves exposing a sample to X-rays and analyzing the resulting diffraction pattern. By measuring the angles and intensities of the diffracted X-rays, the positions of atoms in the crystal lattice can be determined. XRD can provide information about the unit cell dimensions, symmetry, and atomic positions in SnSe. XRD analysis of the as-synthesized and 250°C annealed samples is shown the figure 2. The first peak is formed at the position of 26.36 and the corresponding miller indices (210) the second, third, fourth, fifth, and sixth peaks are respectively formed at positions of 29.28, 39.28,42.99, 47.36, and 48.35, and the miller indices for these positions are (111), (311), (202), (511) and (240) respectively. This diffraction peak matches the standard diffraction peak and corresponds to JCPDS 01-089-0233 and the structure of SnSe is orthorhombic at this temperature. The crystallite size was calculated by the Debye Scherer equation and is 63 nm [13, 14]. The larger the particle size the greater its ability to absorb light [15]. It is noted that with an enhancement in annealing temperature, the grain size has a higher value as can be seen from the XRD graph. The absorbance and conductivity have a direct relation with grain size and this high value of grain size is a characteristic of the absorbing layer.

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

where,
D is the crystallite size
K is the Scherer's constant (k=0.9),
λ is the wavelength of Cu monochromatic kα lines. ( λ =1.54060 $A^0$)
**β** is the peak broadening (**β**=0.25279 rad)
Θ is the peak position (Θ=29.28$^0$) [10].

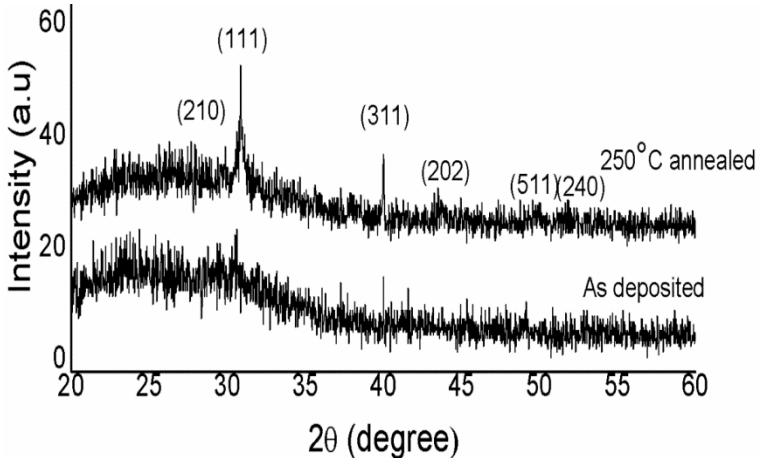


*Fig. 2. XRD analysis annealed at temperature 250 °C.*

The structural parameters for tin selenide annealed thin film are calculated and tabulated in table 1.

*Table 1. Structural parameters of 250℃ annealed tin selenide thin film.*

| No. | parameter | formula | value | reference |
|---|---|---|---|---|
| 1 | Crystalline size (D) | $D = \frac{K\lambda}{\beta \cos(\theta)}$ | **63 nm** | **[16]** |
| 2 | Strain ($\epsilon$) | $\varepsilon = \frac{\beta}{4\tan(\theta)}$ | **11.14** | **[17]** |
| **3** | Dislocation density (δ) | $\delta = \frac{1}{D^2}$ | $2.52\times10^{14}$ m$^{-2}$ | [18] |
| 4 | Number of crystallite per unit area (N) | $N = \frac{t}{D^3}$ | $2.62\times10^{15}$ m$^{-2}$ | [19] |

The transmittance analysis of tin selenide is shown in the following figure 3. The transmission decreases with an increase in the annealing temperature. The transmittance edge increases from 650 nm for the as-deposited to 750 nm for 250°C annealed samples. The transmittance is lowest in the visible region for the annealed sample at a temperature of 250°C. It means that SnSe absorbs nearly all the photons of visible range.

The graph of absorption coefficient measured in cm$^{-1}$ on y-axis and wavelength λ measured in nm on x-axis give us absorption coefficient which is given by the following relation [20].

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

where,
K is the extinction coefficient of the material
and λ is the wavelength measured in nanometers.

The absorbance spectrum of tin selenide (SnSe) thin films typically depends on various factors such as film thickness, crystallinity, and temperature. SnSe is a semiconductor material that exhibits strong absorption in the infrared (IR) to near-infrared (NIR) wavelength range. The absorbance spectrum of SnSe thin films is often measured using techniques such as UV-Vis-NIR spectroscopy. In general, SnSe thin films show high absorption in the mid-infrared (MIR) range,

with a relatively low absorbance in the visible and near-infrared (NIR) regions. The absorbance spectrum typically exhibits a broad peak in the MIR range, which is associated with the characteristic vibrational modes of SnSe crystals [21, 22]. The position, width, and intensity of this peak can vary depending on the film thickness, deposition conditions, and crystal structure.

Additionally, the absorbance spectrum of SnSe thin films can also be influenced by the presence of defects, impurities, and surface roughness. Defects and impurities can introduce additional energy states within the bandgap of SnSe, leading to changes in the absorbance spectrum. Surface roughness can also affect the optical properties of thin films, such as scattering and interference effects, which can result in modifications to the absorbance spectrum. The absorbance of the SnSe is large in visible range which can be observed from the figure. The low band gap of SnSe leads to high absorbance [23]. The absorption coefficient of the sample annealed at a temperature of 250°C is ($2\times10^4$/cm) in the visible spectrum. The absorbing material must have high absorption coefficient such that it may absorb nearly all the photons falling over it. The absorption coefficient of SnSe calculated in this work has a higher value than silicon-based devices.

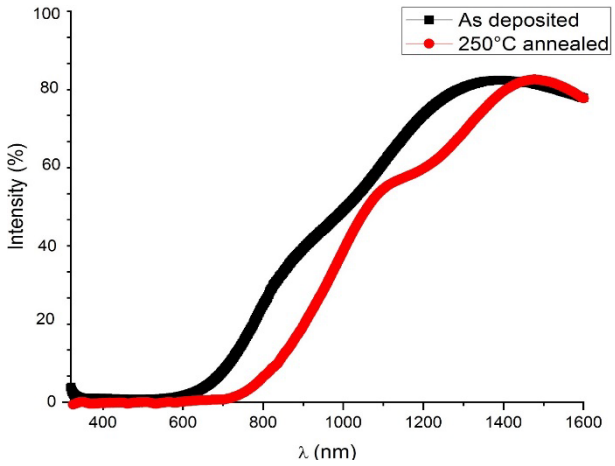


*Fig. 3. Transmittance spectrum of tin selenide (as deposited and annealed).*

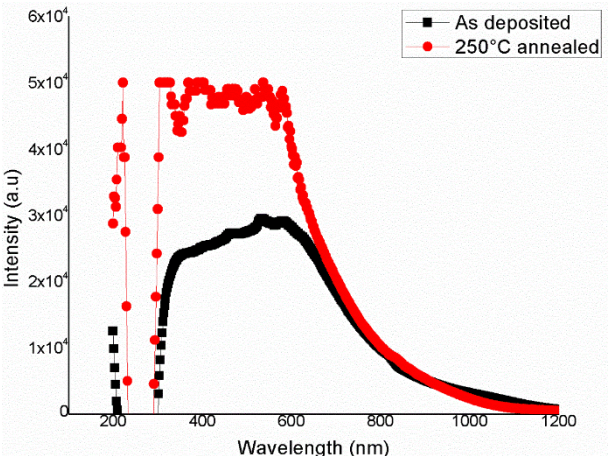


*Fig. 4. Spectrum for absorption coefficient.*

The band gap of tin selenide (SnSe) can be calculated using various methods, such as density functional theory (DFT) calculations, empirical pseudopotential method (EPM)

calculations, and experimental measurements [24, 25]. Experimental techniques, such as optical spectroscopy or electrical measurements, can be used to directly measure the band gap of SnSe. For example, using techniques like UV-Vis-NIR spectroscopy, the absorption edge in the spectrum can be determined, and the band gap can be estimated from the onset of absorption. Electrical measurements, such as temperature-dependent conductivity or Hall effect measurements, can also provide information about the band gap of SnSe. It's important to note that the calculated or measured band gap of SnSe may vary depending on the method used, the level of approximation, and the specific conditions of the calculation or measurement. The band gap is calculated by using the following relation [15, 16, 17].

$$\alpha h\nu = A\,(h\nu - E_g)^n$$

By plotting αhν on the y-axis and hν on the x-axis and using the given relation as in reference [26, 27] we get the value of the band gap. Here α represent the absorption coefficient and h is the planks constant and $E_g$ is the band gap energy. For direct transition n = and for indirect transition n =2 [28]. The value of the band gap reduces with an increase in film thickness. The band gap of the SnSe is obtained by plotting a graph between 2 and. The band gap value can be obtained by extrapolating the linear part of the graph on the x-axis as shown in figure 5. The band gap value that was obtained in the current work is 1.36 eV and 1.28 eV for the as-deposited and annealed sample.

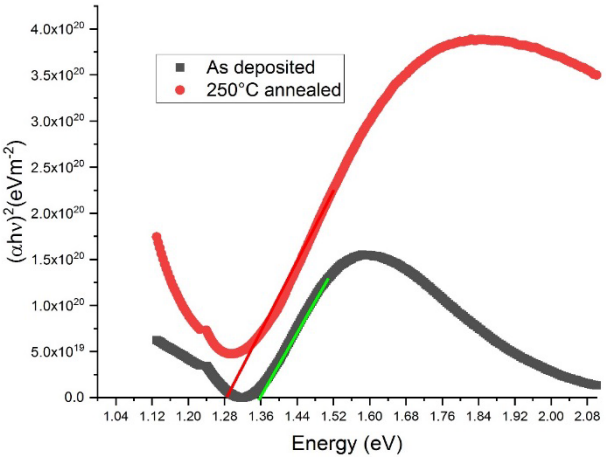


*Fig. 5. Band gap calculation for SnSe as deposited and annealed samples.*

SEM analysis can provide valuable information about the surface morphology, microstructure, elemental composition, and surface modifications of SnSe materials, which can help in understanding their properties and performance for various applications, such as thermoelectrics, optoelectronics, and energy conversion devices [25]. Scanning Electron Microscopy (SEM) analysis is a powerful imaging technique that can be used to investigate the surface morphology, microstructure, and elemental composition of tin selenide (SnSe) materials. SEM analysis involves bombarding the surface of the material with a focused electron beam and collecting the signals emitted from the surface to create high-resolution images. Figs. 6(a) and 6(b) show the SEM images of the as-deposited and annealed samples. The as-deposited thin film in figure 6(a) shows that the SnSe is widely spread with no uniform pattern and most of the textures are still discrete, with only a few features starting to connect with each other. For the annealed sample, all of the texture features are connected with each other to cover the entire surface. Therefore, a zoom-in-top view of a sample figure 6(b) shows the particle size of about 70nm in agreement with the size calculated from XRD. It is obvious in the annealed sample that the grain boundaries have become more peculiar and concentrated which might lead to an enhancement in the carrier concentrations thereby leading to increase in the electrical conductivity of the annealed thin film.

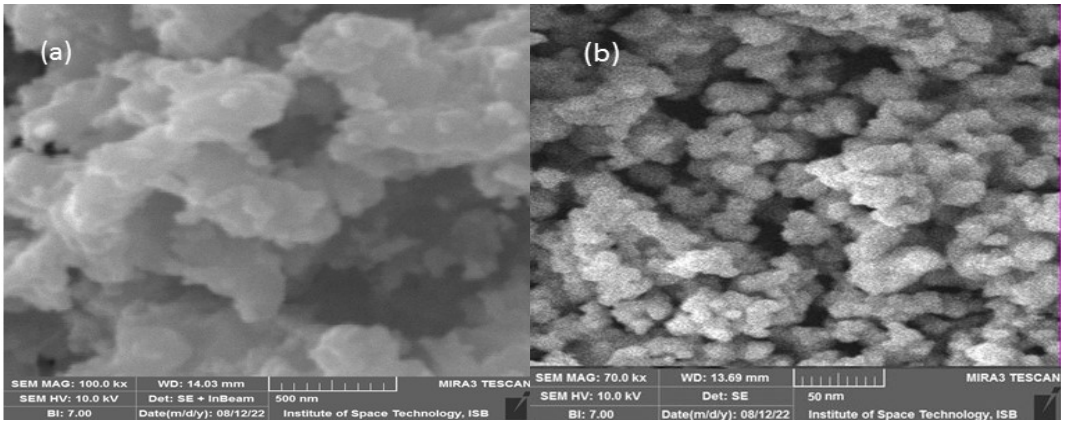


*Fig. 6. SEM images for as deposited and annealed samples.*

Current-voltage (IV) analysis is a commonly used technique to investigate the electrical properties and behavior of tin selenide (SnSe) materials. IV analysis involves measuring the current flowing through a SnSe sample as a function of the applied voltage, which can provide important information about the electrical conductivity, carrier mobility, and device performance. IV analysis of SnSe materials can be performed using different setups, such as two-probe, four-probe, or Hall effect measurements, depending on the specific research or application requirements. For electrical conductivity, IV analysis can provide information about the electrical conductivity of SnSe materials, which is a measure of their ability to conduct electric current. By measuring the current flowing through a SnSe sample as a function of the applied voltage, the electrical conductivity can be calculated using Ohm's law ($\sigma = J / E$), where $\sigma$ is the electrical conductivity, J is the current density, and E is the electric field. IV analysis can reveal the dependence of the electrical conductivity on temperature, doping, or other factors, which can provide insights into the charge transport mechanisms and electrical properties of SnSe materials. The current-voltage graphs for the 250°C annealed and as-deposited SnSe thin films are demonstrated in Figure 7**.** The straight correlations between current and annealing temperatures can be obtained for both the samples with an incremental increase in current with respect to the applied voltage. The rise in the current due to variation in applied voltage is noted for the annealed sample which is an indication of the good semiconductor nature of the SnSe thin film material. The increase in electrical conductivity of the annealed thin film can be attributed to contracting of grain size density and increased grain size due to annealing temperatures leading to enhancement of carrier concentrations.

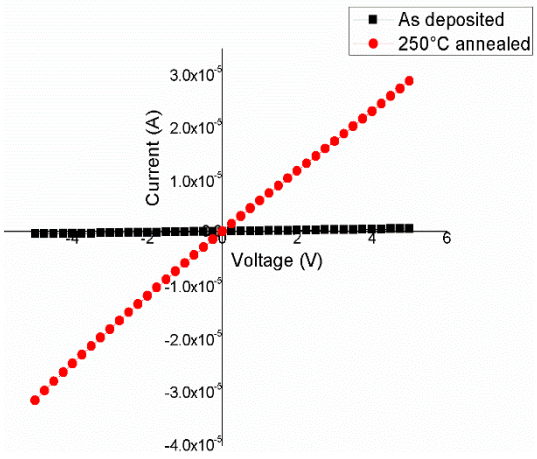


*Fig. 7. The current-voltage characteristics for* tin selenide *thin films.*

## 4. Discussions

XRD analysis can provide information about the crystal structure, crystal phase, and crystallinity of SnSe materials. The XRD pattern of SnSe exhibits sharp diffraction peaks, indicating a well-defined crystalline structure. The positions and intensities of the diffraction peaks was used to determine the crystal phase, lattice parameters, and crystal size. SEM analysis have provided high-resolution images of the surface morphology and microstructure of SnSe materials. The absorption spectrum of SnSe thin films was measured using UV-Vis spectroscopic techniques. The absorption spectrum typically shows the absorption intensity as a function of wavelength, and provided information about the optical band gap, absorption edges, and excitonic transitions in SnSe material. The absorption spectrum also determined the optical properties and band gap of SnSe, which are important for understanding its potential for optoelectronic applications. IV analysis have provided information about the electrical conductivity of SnSe materials. IV measurements revealed the current-voltage characteristics, such as the electrical conductivity and semiconducting behavior of the SnSe material. This study is a step to comprehend SnSe material for its utilization in photovoltaics as an absorber layer.

## 5. Conclusion

The optoelectronic properties of tin selenide semiconductor were studied and compared for photovoltaic application for the as-deposited and at the annealing temperature of 250° C. The SnSe thin film prepared by thermal evaporation technique with ~500 nm thickness has low transmittance in the visible region and absorbs nearly all photons of the visible spectrum. The absorption coefficient of the thin film increases with annealing temperature and is found to be of the order of $10^4$ $cm^{-1}$ for a 250°C annealed sample. The band gap of tin selenide thin films is 1.36 eV and 1.28 eV respectively for the as-deposited and annealed sample. The IV characteristics confirm the ohmic behavior of tin selenide thin films.

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