



SnSe Semiconductor Films: Sputtering and Analysis of the Effects of Substrate Temperature on Their Optical Properties

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ABSTRACT: This study examined the preparation of SnSe semiconductor films using thermal sputtering on glass slides, while examining the effects of temperature (100-300)°C and pressure (1-1.5) bar on their properties. Optical results (using UV-VIS) showed a gradual improvement in light transmission and film quality with increasing temperature, indicating a reduction in structural defects. At low temperatures (100)°C, the absorbance was high due to defects, while transparency improved at 150°C. Temperatures 200 and 250°C showed greater crystalline regularity. At 300°C, the absorbance reflected typical semiconductor behavior, demonstrating the effect of temperature on the energy bandgap and atomic rearrangement, enhancing their suitability for advanced optical and electronic applications such as lasers and solar cells.

KEYWORDS: semiconductor thin films, sputtering, optical properties, tin-selenide,

INTRODUCTION

Tin selenide (SnSe) has emerged as a futuristic semiconductor material for various optoelectronic applications due to its favorable properties, including an appropriate band gap, high absorption coefficient, and environmental stability. Several comprehensive review studies have examined the progress and potential of SnSe thin films. SnSe have exceptional thermoelectric properties, with studies showing record-high thermoelectric figure of merit (ZT) values[1]. The material's layered crystal structure and anisotropic properties make it particularly attractive for energy conversion applications. Reviews have emphasised the various synthesis methods for SnSe thin films, including thermal evaporation, chemical vapour deposition, sputtering, and solution-based techniques, each offering distinct advantages for different applications[2]. Co-evaporated SnSe films (490 nm thickness) demonstrated controlled optoelectronic properties through facile thermal coating methods, providing a foundation for later advancements in thin-film engineering. The band gap assessed from absorption spectra for the highly annealed sample was 1.52 eV. The resistivity and sheet resistance were measured with four-probe techniques and the sheet resistance was $\sim 1.362 \times 10^4$ ohm for the highly annealed film[3]. Annealing SnSe thin films results in increased band gap values and larger grain sizes, as well as improved crystallinity. For example, band gaps can increase from 1.5eV to 2.2eV with higher annealing temperatures, and grain sizes can grow from 60nm² to 95nm². This ability to tune properties is advantageous for customizing films for specific optoelectronic applications [4]. The high absorption coefficient and tunable band gap make SnSe thin films suitable for solar cells. Their low transmittance and high absorption efficiency are critical for maximizing light harvesting [5]. SnSe/MoS₂ heterostructures exhibit strong current rectification and photovoltaic behavior, achieving short-circuit currents of 67 nA and photon-electron conversion efficiency of 1.8%, with photoresponsivity up to 384A/W, indicating potential for ultra-sensitive photodetection [6].

TIN-SELENIDE STRUCTURE

Tin-selenide (SnSe) is a semiconductor material known for its optical properties. SnSe at room temperature has an orthorhombic crystal structure, specifically the α -SnSe phase with space group Pnma. This structure is layered and characterized by two SnSe sheets oriented in the (0,0,1) direction, held together by Van der Waals forces [7], (see figure 1).

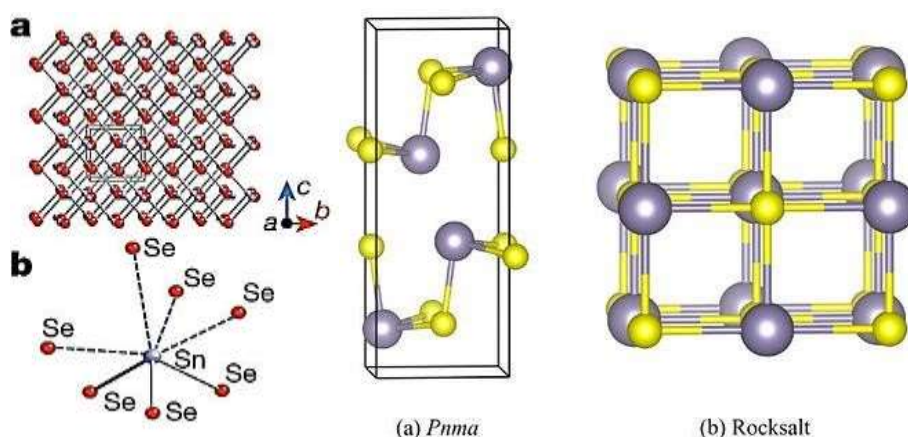


Figure (1): Tin selenide structure

In this compound, tin (Sn) and selenium (Se) atoms interact through their valence electron configurations. Selenium is more electronegative than tin, causing selenium atoms to acquire two electrons from tin atoms. This changes the electron configuration of tin from $4d^{10}5s^25p^2$ to $4d^{10}5s^25p^0$, while the electron configuration of selenium becomes $4s^24p^6$. The sp^2 hybridization leads to a wrinkled surface, where each atom forms three covalent bonds with three neighboring atoms. Consequently, tin attains a +2 oxidation state (Sn(II)) because its 5p electrons are involved in bond formation, while the 5s2 electrons occupy a non-bonding orbital. The presence of a lone pair of tin (5s) electrons significantly distorts the crystal structure. The overlap between the lone pair of tin and selenium ions creates an anti-bonding combination that favors pairing between the 5s and 5p electrons of tin, resulting in an energetically asymmetric electron density.

As we move from oxygen (O) to sulfur (S) and then to selenium (Se), the interactions between the upper p orbitals of the anions and the tin orbitals decrease. This reduction leads to a lower asymmetric density and influences the level of distortion in the electronic structure [8]. The structure known as herzenbergite, which does not align well with the strong asymmetry of tin oxide (SnO), is compatible with tin in SnS and SnSe. The lone pair of tin (5s) electrons can also indirectly affect the separation between layers. The unit cell consists of eight atoms arranged in two adjacent layers that are perpendicular to the long axis. The local atomic arrangement of tin atoms resembles a distorted octahedron. Each atom forms six heterogeneous bonds: three stronger bonds with its nearest neighbors in the same double layer and one bond with an atom in the adjacent double layer, which helps hold the double layers together. The crystal structure of SnSe is orthorhombic and exhibits a layered arrangement, following the Pnma space group. This structure can be viewed as a distorted rock salt phase. Different perspectives of the structure along the a, b, and c crystallographic axes reveal its anisotropic nature. Some of its key physical properties include a melting point of 861°C, and a direct band gap of 1.3eV. Its thermal conductivity is about 0.46-0.7 W/m-K, and it exhibits p-type or n-type conduction, [9].

This study focuses on preparing thin films of SnSe semiconductor using the sputtering method at various substrate temperatures, analyzing how temperature variations affect the optical properties.

MATERIALS and METHODS

(i) The substrate used as the basis for building the films which are ordinary glass slides 1 mm thick, 2.5cm x 7.5cm. Cleaning the glassware involves several steps. The glassware is washed in hot distilled water for two minutes or more, then washed in methanol for two or three minutes using ultrasound. It is then washed again in distilled water for two or three minutes and then washed in acetone for two or three minutes using ultrasound. It is then washed again in distilled water for two minutes. Finally, it is dried in an air dryer, thus preparing it for the deposition process.

(ii) Preparation of solutions used in the deposition of SnSe films:

- 1) Dissolve 2.5gm of sodium sulfide (Na_2SO_3) in 3.5 ml of distilled water with 0.85gm of selenium (Se) for two hours in a magnetic stirrer at 170°C. The solution is then filtered using filter paper to remove the precipitates.
- 2) Dissolve 1.8gm of tin chloride ($SnCl_2$) in 20ml of distilled water, adding a few drops of ammonia to maintain the basicity of the solution until it reaches pH=12 or pH=11.5.
- 3) Mix the two solutions in paragraphs (1 and 2) above for 15 minutes to obtain a black or coffee-colored solution.
- 4) Using the spray system shown in Figure 2, the solution was sprayed onto glass slides of the prepared and organised samples. Ten sprays were performed from a distance of 30 cm at different temperatures (100, 150, 200, 250, 300)°C and different pressures (1 and 1.5 bar).

(iii) Thermal spray deposition was done using the thermal spray system, as shown in Figure 2:

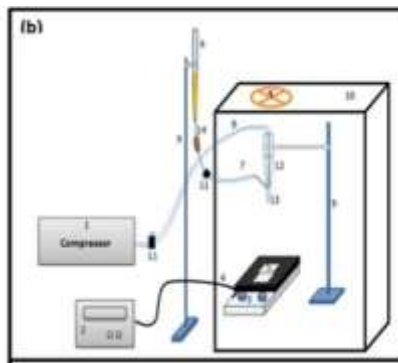


Figure (2): The thermal spray system

The samples prepared at different temperatures (100, 150, 200, 250, 300)°C. some it were shown in Figure 3.

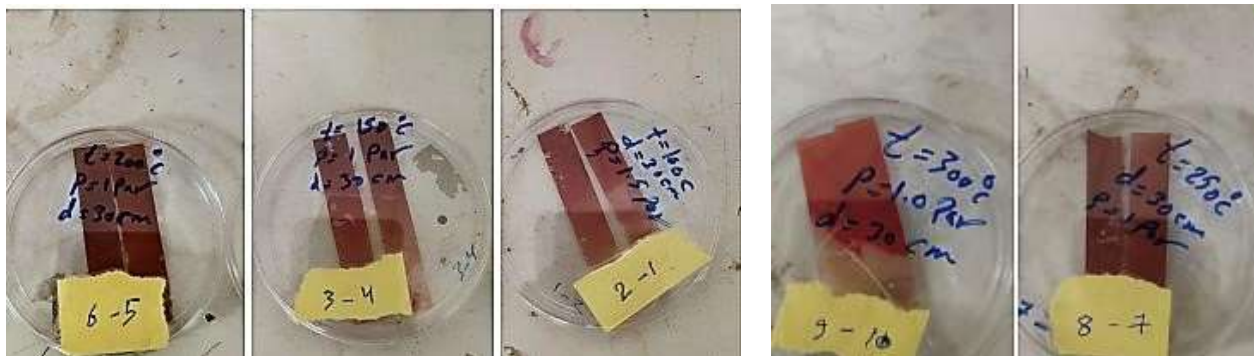
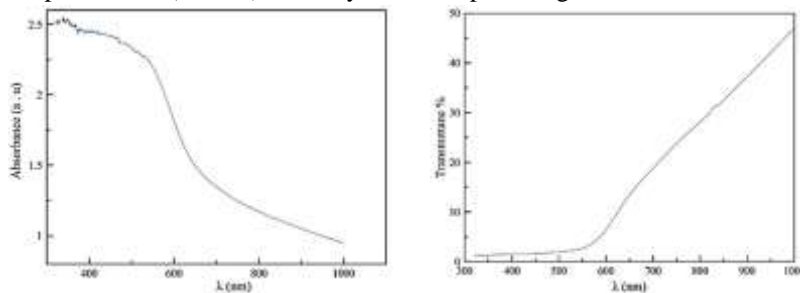


Figure (3): Samples of the prepared SnSe at different temperatures

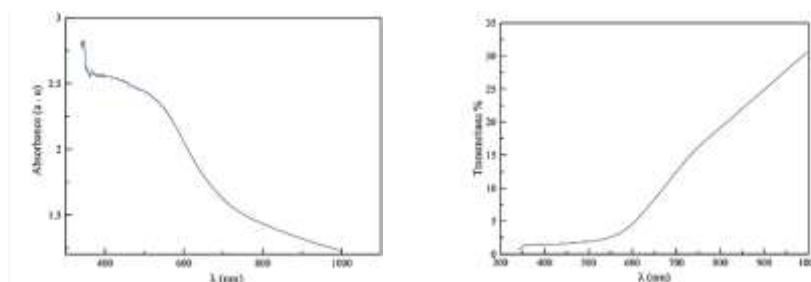
- (iv) Optical Measurements: The optical properties of the samples were tested using the UV-VIS device shown in Figure 4. Absorbance and transmittance were measured, and the band gap energy was calculated using Taue's relation [10]: $(\alpha h\nu)^2 = A(h\nu - E_g)$.

RESULTS and DISCUSSION

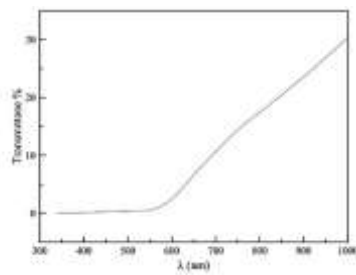
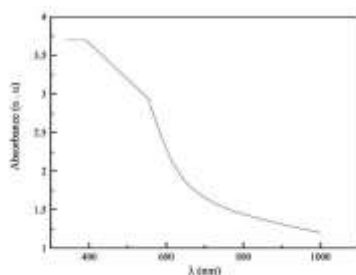
Figure (4) shows the absorbance (a) and transmittance (b) of the samples of SnSe films prepared at temperatures of 100,150, 200, 250, and 300 °C under a pressure of (1.5 bar). Notably, the absorption edge occurs at the wavelength (540 nm).



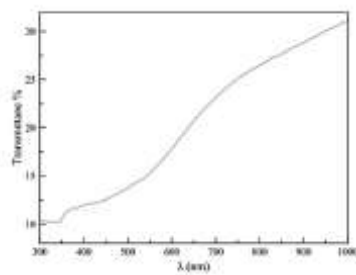
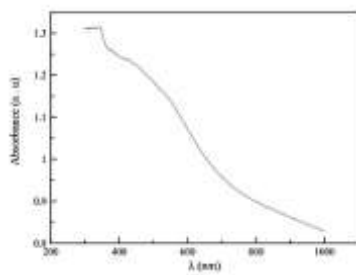
(a) absorbance and (b) transmittance for the prepared sample at 100°C



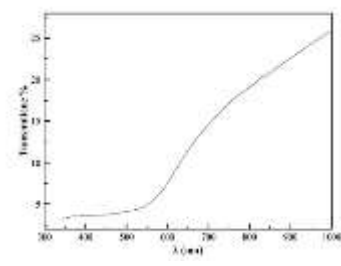
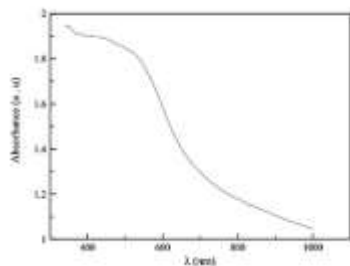
(a) absorbance and (b) transmittance for the prepared sample at 150°C



(a) absorbance and (b) transmittance for the prepared sample at 200°C



(a) absorbance and (b) transmittance for the prepared sample at 250°C



(a) absorbance and (b) transmittance for the prepared sample at 300°C

Figure (4): illustrate the absorbance (a) and the transmittance (b) of the SnSe samples films prepared at 100,150, 200, 250, and 300 °C

Figure 4, shows the transmittance and absorbance behaviour of SnSe prepared at different temperatures, reflecting the effect of thermal changes on the optical properties of these thin films. At a relatively low temperature (100°C), transmittance is low in the ultraviolet range, then begins to gradually increase at visible and near-infrared wavelengths. This behaviour is explained by the presence of high absorption at short wavelengths, which is an indicator of a favourable energy gap. The high absorption is likely related to an imperfect crystal structure or crystal defects that increase the absorption of high-energy photons. This phenomenon may be due to a low preparation temperature, which leads to the formation of films with an imperfect structure, which negatively affects transmittance. When the temperature is increased to 150°C, a clear improvement in the quality of the material is evident, as crystal defects are reduced, allowing more light to pass through, thus increasing transmittance. The absorbance gradually decreases with increasing wavelength, making these films more suitable for applications requiring high transparency, such as smart windows or transparent layers in optical devices. However, an improvement in the crystalline structure was observed at 200°C, where the transmittance continues to gradually increase with increasing wavelength, indicating an improvement in the material's transparency. This may be attributed to the interaction between high-energy photons and the material's energy gap, where absorption is high at short wavelengths due to the high photon energy being aligned with the energy gap. However, increasing temperature leads to improved crystallinity and a reduction in crystalline defects, which reduces the absorbance and increases the transmittance, making the material more suitable for applications requiring high transparency, such as optical layers and photonic systems. When the temperature is raised to 250°C, the transmittance behaviour is similar to that observed at 200°C, but with a slight increase in the overall transmittance. This is explained by the improved crystallization quality and reduced structural defects, which reduce internal scattering of light. In contrast, the absorbance generally decreases with increasing temperature, which can be explained by the improved regularity of the crystal structure, thus reducing absorption sites. At the preparation temperature (300°C), the absorbance curve exhibited a behaviour characteristic of semiconductor materials, where the absorbance is low at long wavelengths (1000 nm) and gradually increases with decreasing wavelength, reaching high values at short wavelengths

(approximately 400 nm). This reflects a temperature-sensitive behaviour of the optical energy gap, where increasing temperature leads to atomic rearrangement and improved crystal structure, slightly affecting the energy gap.

CONCLUSION

Increasing the temperature can enhance crystallisation within the material, resulting in more regular and larger crystals. This improvement helps to reduce structural defects, which can negatively impact the optical gap energy. Additionally, altering the ratio of tin (Sn) to selenium (Se) influences the stability of the material. It was also noted that the difference in the coefficients of thermal expansion between the thin film and the substrate can induce thermal stress, leading to variations in the optical properties of the material. The values of the gap energy fluctuated, reflecting the effects of crystallisation and stress on this energy. Further influential mechanisms were observed during the film preparation process. For instance, annealing, or heat treatment, can enhance crystal quality; however, excessively high temperatures may result in the formation of new defects. At elevated temperatures, the lattice expands, leading to a decrease in gap energy due to lower phase density.

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