Investigation on structural, optical, morphological, and electrical features of nanocrystalline SnSe thin films synthesized by low-cost method

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***Abstract*: With the help of X-ray diffraction (XRD), the films' structure and crystalline size are determined. The surface morphology of the films was investigated by using scanning electron microscopy (SEM). Energy dispersive X-ray analysis (EDAX) coupled with SEM was used to determine the elemental composition of the films. According to X-ray diffraction analyses, The films were multi-crystalline, showing an orthorhombic structure with the most pronounced grain alignment along the (111) and (112) axes. Studies using scanning electron microscopy demonstrate that tiny grains were combined to create a collection of larger sizes. The Debye-Scherrer formula estimated that the produced SnSe films had crystallite sizes of roughly 30 nm. According to EDAX analysis, the produced films were almost stoichiometric. SnSe thin Films are deposited using a chemical bath deposition method.**

***Keywords*: Semiconductor, Thin films, Tin Selenide, XRD, SEM, and EDAX.**

1. Introduction:

A significant direct band gap semiconductor material with an orthorhombic structure and energy band gap of 1 eV is tin selenide (SnSe). Because it might be utilized in memory-switching, photovoltaic, and light-emitting devices. SnSe has been drawing a lot of attention. Binary semiconductors are considered important technological materials because of their potential applications [1-4]. The methods used to create thin films of tin chalcogenide have received a lot of attention from various researchers. In the recent past, For many different purposes, colloidal semiconductors have been chemically deposited to create semiconductor thin films. Tin selenide (SnSe) is a binary, anisotropic IV-VI semiconductor with a tiny band gap. It works well for solar energy conversion since it has an energy gap of roughly 1.0 eV [5].

In the current study, a simple chemical technique has been used to try and develop SnSe films on a glass substrate. This method's main benefit is that it is very straightforward and cost-effective, requiring simply solution containers and substrate mounting tools. Regarding varied deposition times, the structural, morphological, and electrical characteristics of the deposited layer were investigated. By using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), and Hall Effect measurement techniques, structural, elemental, morphological, and electrical features of the formed films were investigated.

In the current work, a chemical bath deposition approach has been used to try and develop SnSe thin films on a glass substrate. This technique does not require sophisticated instrumentation and is a convenient way for large-area deposition. We have used tin chloride and sodium selenosulphate as originators of Sn^{2+} and Se^{2-} ions in the reaction system.

2. Experimental Procedure

2.1. Synthesis of SnSe films

The bath container was a 100 cc beaker. The substrates utilized were 75 mm × 25 mm x 1.35 mm Corning microscope glass slides. The glass sides were preserved in a 0.1% SnCl2 solution after being first cooked in chromic acid and then cleaned with deionized water. Finally, deionized water was used to clean the glass plates, and they were then air-dried before the deposition procedure.

Preparation of stock solutions:

- Sodium Selenosulphate solution (1M)

8.5 g of selenium was added to a solution of 25 g of sodium sulfite in 350 ml of water. The solution was continuously stirred while being refluxed for 8 hours at 900 C. A dark, airtight bottle was used to store the sodium selenosulphate filtrate after the solution had been cooled and filtered [6].

$Na_2SO_3 + Se == Na_2SeSO_3$

- 1M solutions of sodium hydroxide were prepared in deionized water.

In a 100 ml beaker, 1.8 grams of $SnCl_2$ was dissolved in 20 ml of water. 1 M NaOH solution was then added dropwise to the mixture until the pH reached 11.5 and the reaction was complete. After that, 20 ml of sodium selenosulphate was added. SnSe films were deposited on corning glass slides in the aqueous alkaline bath using sodium selenosulphate and tin chloride as precursors of Se^{2+} and Sn^{2+} ions respectively. At an ideal constant temperature, a good quantity of tin selenide (SnSe) films was accumulated over periods of 60 min, 90 min, 120 min, and 150 min respectively.

2.2. Film Characterization

Using CuK radiation with a wavelength of 1.5418 0A, the XRD patterns of films were recorded by using Philips (PW 1140/09). EDAX connected to a JEOL scanning electron microscope was used to determine the elemental composition of the films (SEM). Ecopia Corp. HMS- 5000 sets were used to measure the hall effect on the films.

3 . Results

An alkaline bath containing Sn^{2+} and Se^{2-} ions was used to create SnSe films. Tin selenosulphate complexes are created in greater amounts than selenosulphate. When selenosulphate hydrolyzes in an alkaline media, selenide ions are gradually released. SnSe is then precipitated when the selenide ions are combined with the tin ions that were also liberated during the hydrolysis of the tin selenosulphate complexes [7]. According to research, the film begins to grow after an initial nucleation period of roughly 60 minutes. On the substrate, timeless material production is seen as the deposition rate increases.

4. Discussions.

With the help of a stylus profile meter, the film's thickness was determined. The thin film thickness change with deposition time is shown in the table. The film's thickness first grows as the deposition time lengthens. After 120 minutes, the film thickness drops as the formed film dissolves in the excess complexing agent in the bath, reaching a maximum of 220 nm.

X-ray diffraction provides insightful data on the many crystallographic facets of the thin film. Figure 1 depicts the XRD pattern at a 120-minute deposition time. Strong peaks in the XRD arrangement are a representation of the films' polycrystalline nature. The creation of well-crystallized films is indicated by the strong and precise diffraction peaks. The observed d-values and the accepted values for the orthorhombic arrangement of SnSe correspond quite well. The (111) and (112) orientations have the strongest intensity. Zainal et al. and Kumar et al. [8] both report similar peaks [9].

4.1 XRD analysis

The X-ray diffraction (XRD) pattern of SnSe films is shown in Fig. 1 and was recorded at room temperature. X-ray diffraction provides insightful data on the sample's numerous crystallographic characteristics. The polycrystalline character of the films is represented by strong peaks in the XRD pattern. The creation of well-crystallized films is indicated by the strong and precise diffraction peaks. The experimental d-values for the SnSe alloy were determined using Bragg's relation 2dhkl sin h 14 nk by obtaining h values from the peaks of the XRD patterns. The observed d-values for the orthorhombic structure of SnSe are closely matched by the conventional values. The XRD pattern in the current study shows the presence of prominent peaks matching the material's planes (210), (111), (102), (020), (112), (221), (402/420), and (800), with the intensity of (111) and (112) orientation being the most pronounced (evaluated by texture coefficient). For SnSe films, Kumar et al. [11] and Zainal et al. [12] reported that the (111) plane is the optimal orientation. Mathews et al. similarly found a similar outcome using the (111) plane's preferred orientation. The normal crystallite size was determined by determining the strong peak. In the current experiment, SnSe crystallites were assessed to be 28 nm in size. For almost stoichiometric orthorhombic SnSe films, The calculated lattice parameters were found to be a = 11.49 A^0, b = 4.14 A^0, and c = 4.42 A^0, which are in good agreement with the values that have been reported[12]. Using the relation, the dislocation density (d) for the (111) plane is computed as the length of disorder lines per unit volume of the crystal. The relationship was used to determine the microstrain that was generated in the film:

In the current work, the disorder density and form of SnSe films were determined to be between 12.7 (1014 lines/m2) and 8.9 respectively (10-4 lines-2 m-4). Improved stoichiometry, which is attained by SnSe thin films with minor strain and disruption density, is what causes the volumetric expansion of thin films. [13].

4.2 EDAX analysis

Using the EDAX process, produced SnSe films underwent a quantitative analysis. The EDAX spectra of SnSe films are displayed in Figure 2. Only the elements Sn and Se were subjected to the elemental analysis. Estimates indicate that the Sn and Se elements have constituent atomic percentages of 49.8 and 50.2%, respectively, which is similar to the substance's original makeup (Sn and Se make up 50% of the total). A quantitative study of the spectrum reveals that the produced SnSe films have an atomic composition that is close to 1:1 stoichiometry. The reports from Mariappan et al. and this EDAX results are in good accord. [13].

4.3 SEM analysis

Figure 3 shows the micrography of SnSe films created on a glass substrate at an ideal temperature using a scanning electron microscope (SEM). One can deduce from the micrography that smaller crystallites coalesced into a group with an average size of 30 ml. According to the image J program, each crystallite had a size of about 28 nm, which is nearly the same as the particle size predicted by the Scherer formula using the XRD data. Additionally, weak porosity was seen and the crystallite borders were not clearly defined.

4.4 Raman analysis

Fig. 4 details the Raman spectrum of the SnSe film formed using the CBD (Chemical bath deposition) technique. We looked at three broad bands at 32, 113, and 255 cm^{-1}. The calculations based on group theory predict Raman bands at 35, 72, 134, and 152 cm^{-1} The single band that was detected in our example at 113 cm^{-1} corresponds exactly to the band that group theory anticipated for B_3g symmetry. The presence of amorphous selenium is shown by the band at 255 cm^{-1}. [14]. The final band seen at 32 cm^{-1} is unclearly attributed, but Ag symmetry is most likely to blame. A decrease in crystal symmetry and a change in unit cell characteristics are to blame for the appearance of this band. Additionally, additional research is required to confirm the band's origin[12, 15].

4.5 Optical analysis

Reflection spectra were used to calculate the energy band gap of these films [16, 17]. Assimilation constant a and the energy band gap (Eg) are provided by (reference Tauc relation) $(\alpha h\upsilon)^n =$ c (h$\upsilon - E_g$) ---- (4)

where n describes the modification process and has values of 1/2 and 3/2 for direct allowed and prohibited transitions respectively, and hυ represents photon energy.

4.6 Electrical analysis

Determining the extent of the material's utility value depends in large part on the research of electrical transport. The factors affecting the electrical characteristics are thickness, composition, substrate temperature, and deposition rate. The analysis of electrical transport has a significant role in determining the electrical conductivity (DC) in darkness and underwater, as well as the material's utility value. The factors that affect the electrical properties include composition, substrate temperature, thickness, and deposition rate. Utilizing the two-probe setup, the electrical (DC) conductivity of produced SnSe films at optimum temperature was measured in the temperature range of 300-473 K both in the dark and under light (photoconductivity). Utilizing the two probe setup, illumination of produced SnSe films at optimal temperature was captured between 300 and 473 K. The film's dark conductivity and photoconductivity were plotted as log (conductivity) vs 1000/T and were found to be 0.27 and 0.24 eV, respectively. This value is quite similar to the stimulation energy reported in earlier findings on SnSe films. These graphs' straight lines imply that the predominant conduction mechanism is grain-boundary restricted conduction. The defects brought on by the fact that films are polycrystalline result in grain boundaries.

5. Conclusions. The SnSe films were deposited using an easy and cost-effective technique (Chemical bath deposition). EDAX analysis verified the elemental composition's existence. According to SEM analysis, a group of particles with an average size of 30 m was put together. The SnSe phase is confirmed by Raman analysis. The photoconductivity and dark conductivity revealed the materials' semiconducting characteristics. According to the study, deposition time has a significant impact on the growth and structure of the films. The polycrystalline nature of the films is evident from XRD. With longer deposition times, agglomeration takes over as the dominant process. With time, it was discovered that the crystallite size grew. These findings demonstrate the technique's and the material's high potential, making these films appropriate for applications in technologically significant devices.

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Figure and Table captions

Figure. 1 X-ray diffraction pattern of SnSe film
Figure. 2 EDAX spectra of SnSe film
Figure. 3 Scanning electron micrographs of SnSe film
Figure .4 Raman spectra of SnSe film
Figure. 5 Energy band gap determination of SnSe film from reflection spectra
Figure. 6 Plot of log (conductivity) versus 1000/T of SnSe film

Tab.1

Duration of Deposition (min)	60	90	120	150
Thickness (nm)	80	150	220	180

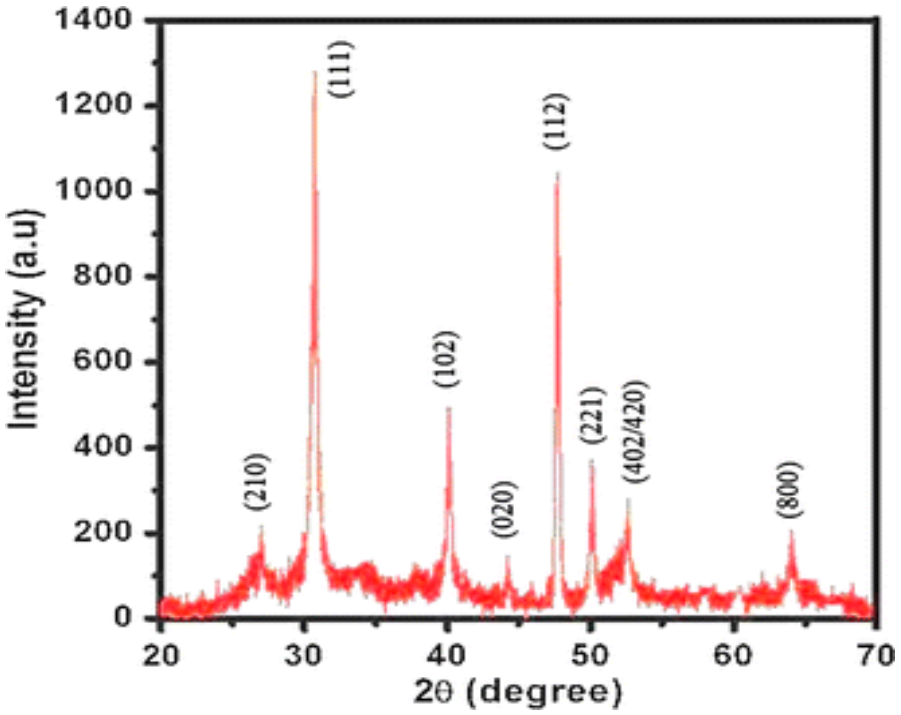


Figure. 1

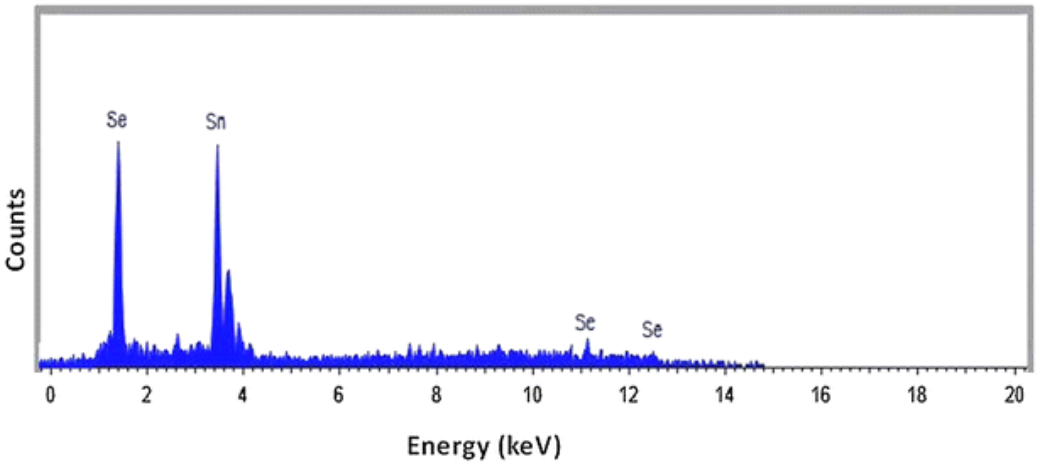


Figure. 2

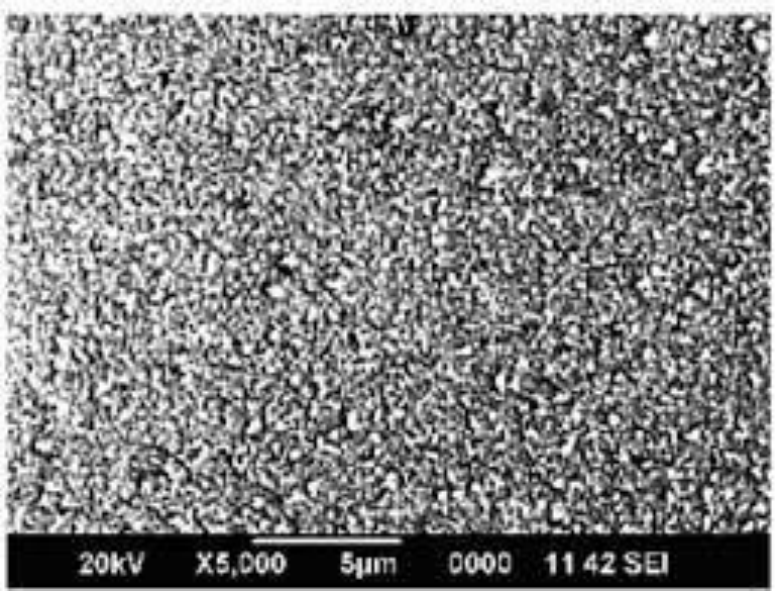


Figure. 3

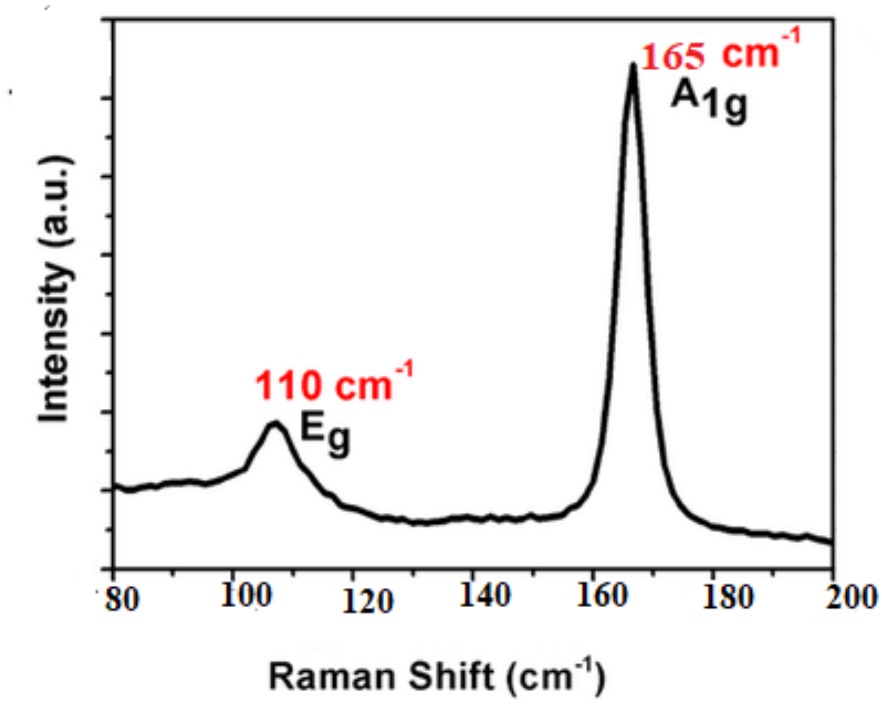


Figure .4

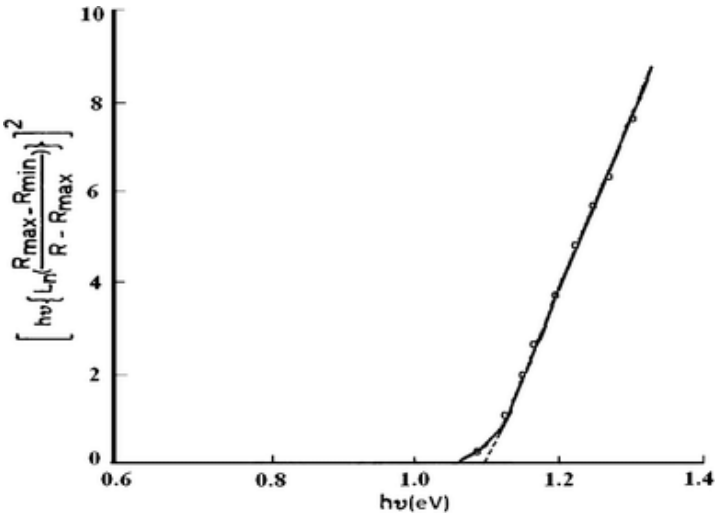
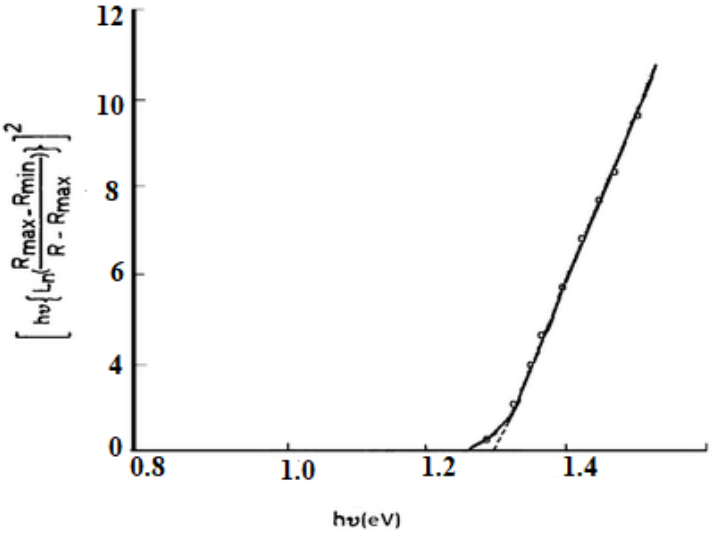


Figure. 5



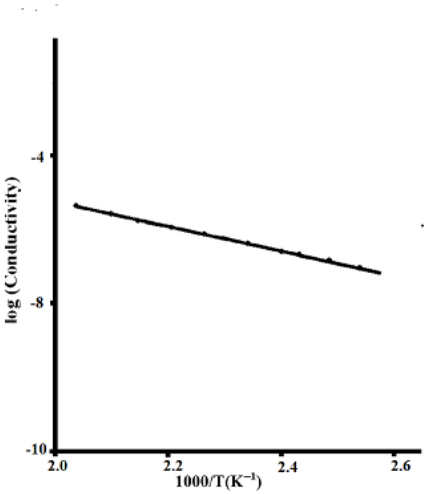


Figure. 6