Structural and optical characterization of reactive evaporated tin diselenide thin films

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Abstract. Tin diselenide thin films with thickness of the order of 300 nm are deposited on glass substrate at a substrate temperature of 523±5 K and pressure of 10^{-5} mbar using reactive evaporation, a variant of Gunther’s three temperature method. High purity tin (99.999%) and selenium (99.99%) were used as the elemental starting materials. The deposited film is characterized structurally using X-Ray Diffraction (XRD). The structural parameters such as lattice constant, particle size, dislocation density, number of crystallites per unit area and strain in the film are evaluated. Optical absorption spectrum of the film is analysed using UV-Vis-NIR Spectrophotometer.

1. Introduction
The study of binary IV-VI compound semiconducting thin films has attracted the attention of researchers due to their suitable physical properties, abundance and low environmental impact of their constituent elements. These compounds in bulk and thin film form have been studied for their electro-optical properties. High absorption coefficient makes them good absorbers for thin film photovoltaic devices. SnSe₂ is a layered semiconductor of IV-VI family with widespread applications in photovoltaic and infrared optoelectronic devices, radiation detectors, holographic recording systems, electrical switching and polarity dependent memory switching devices [1]. Several methods such as Molecular Beam Epitaxy [2], Selenization of sputtered tin layers [3], Thermal evaporation [4], Elemental layer heating [5] and Chemical Vapour Deposition [6] are used for the preparation of SnSe₂ thin films. Compared to other IV-VI compounds SnSe₂ thin films have received relatively less attention. Hence in this paper we preset our results concerning the preparation of SnSe₂ thin films by reactive evaporation. Results on structural and optical properties of these films are also reported.

2. Experimental details
Thin films of SnSe₂ are prepared by reactive evaporation which is a variant of Gunther’s three temperature method [7]. For many binary systems it has been found that the deposition of stoichiometric compound layers by simultaneous evaporation of individual components is possible only by selecting a suitable substrate temperature and adequate incident rates for the components [8].

In the present work, a conventional vacuum system operated in the range of 10^{-5} mbar is used for the preparation of SnSe₂ thin film. Ultrasonically cleaned optically flat glass slides are used as the substrates and are mounted on a substrate holder with a heating arrangement. The temperature of the...
substrate is measured using a fine wire chromel-alumel thermocouple. When the required substrate temperature 523±5 K is attained, high purity selenium (99.99%) from a glass crucible kept in a molybdenum basket is evaporated. When sufficient flux of selenium is obtained high purity tin (99.999%) from a molybdenum boat is evaporated in the atmosphere of selenium. Rate of evaporation of tin and selenium is controlled by the amount of current that passes through the sources. When sufficient fluxes of tin and selenium are attained the shutter kept above the sources is removed so that the vapours of individual elements reach the substrate and react to form the compound film on the substrate surface. Unreacted elemental atoms or molecules will re-evaporate from the substrate surface due to its elevated temperature. Source and substrate temperatures are properly controlled throughout the film deposition so as to obtain good quality SnSe₂ thin films.

3. Results and Discussion

3.1. Structural Characterization

X-Ray Diffraction (XRD) analysis is carried out using Rigaku D MaxC X-Ray Diffractometer for 2θ varying from 10° to 70° with CuKα (1.5404 Å) as the radiation source. The XRD pattern of the as prepared SnSe₂ thin film is shown in figure 1.

![XRD pattern of the as prepared SnSe₂ thin film.](image)

The d values of the prepared film obtained from XRD study well matched with that of SnSe₂ in standard JCPDS (FileNo.23-0602). Comparison of d values of the as prepared film with that of standard d values is shown in table 1. The prepared film is polycrystalline in nature with preferential orientation along the (101) plane. The structure of SnSe₂ is hexagonal. The calculated values of lattice constants are \(a = 3.78 \, \text{Å}, \ b = 3.78 \, \text{Å}, \ c = 6.13 \, \text{Å}.\)
Table 1. Comparison of observed $d$ values of the as prepared SnSe$_2$ thin film with standard $d$ values.

| Observed Value | Standard Value (JCPDS File No.23-0602) | \(hkl\) |
|----------------|----------------------------------------|--------|
| $d$ (Å)        | Relative Intensity | $d$ (Å) | Relative Intensity |
| 6.13           | 18                      | 6.14    | 20                | (001) |
| 2.89           | 100                     | 2.91    | 100               | (101) |
| 2.38           | 7                       | 2.25    | 45                | (102) |
| 2.05           | 5                       | 2.05    | 12                | (003) |
| 1.83           | 5                       | 1.82    | 12                | (111) |
| 1.44           | 5                       | 1.45    | 12                | (202) |

Particle size is calculated as 35 nm using Scherrer formula

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$

where $\lambda$ is the wavelength of the X-Ray used, $\beta$ is the full width at half maximum and $\theta$ is the Bragg’s angle [9]. Dislocation density is estimated as $8.16 \times 10^{10}$ lines cm$^{-2}$ using the relation [9]

$$\rho = \frac{1}{D^2}$$

The number of crystallites $N$ per unit area is estimated as $69.97 \times 10^{10}$ cm$^{-2}$ using the relation [9]

$$N = \frac{t}{D^3}$$

where $t$ is the thickness of the film.

The strain is calculated as $1.65 \times 10^{-3}$ using the expression [9]

$$S = \left(\frac{1}{\sin \theta}\right) \left[ \frac{\lambda}{D} - \beta \cos \theta \right]$$

3.2. Optical Characterization

Absorption coefficient $\alpha$ varies with the photon energy $h\nu$ as

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

for direct transitions in which $n$ is a constant that determines the type of electronic transition causing the absorption and can take values 1/2 and 3/2 for direct allowed and direct forbidden transitions respectively and as

$$\alpha h\nu = B(h\nu - E_g \pm E_p)^n$$

for indirect transitions in which $n$ can take values 2 and 3 for indirect allowed and indirect forbidden transitions respectively where $E_g$ is the band gap energy, $E_p$ is the phonon energy, $\nu$ is the frequency of the incident beam, $A$ and $B$ are constants [10]. Optical absorption of the film is recorded in the wavelength range 2500 nm to cutoff using JASCO V570 UV-Vis-NIR spectrophotometer. Plot of $(\alpha h\nu)^2$ vs $h\nu$ is shown in figure 2. In the absorption data of SnSe$_2$ thin film the best fit is for $n = 1/2$ and it suggests that the transition is a direct allowed one. The straight line portion of the plot is extrapolated to obtain the optical band gap of the film and it is found to be 1.4 eV. Amalraj et al [11] reported an optical bandgap of 1.4 eV for SnSe$_2$ thin films prepared by spray pyrolysis technique at an optimized substrate temperature of 523 K.
4. Conclusion
Good quality thin films of tin diselenide are successfully deposited onto glass substrate under optimized deposition conditions using reactive evaporation. XRD study reveals that the films formed are polycrystalline in nature. Structural parameters such as lattice constant, particle size, dislocation density, number of crystallites per unit area and strain in the film are estimated. The film showed a direct allowed transition with a band gap of 1.4 eV.

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