Optical properties of SnTe$_x$Se$_{1-x}$ thin films

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Ternary alloys of SnTe$_x$Se$_{1-x}$ (0≤x≤1) were synthesized by direct fusion method. The SnTe$_x$Se$_{1-x}$ films were prepared by thermal evaporation under vacuum of about 10$^{-4}$ torr and with evaporation rate of about 30 nm/min. X-ray diffraction and microprobe analysis technique, investigated the structural and the composition analysis of SnTe$_x$Se$_{1-x}$ in powder and thin film forms, respectively. X-ray diffraction patterns of the as-deposited and the annealed films of this system reveal that, these have polycrystalline nature of orthorhombic structure for alloys with compositions x = 0, 0.2, and 0.4 and cubic structure for alloys with compositions x = 0.6, 0.8 and 1. The variation of lattice parameters with different compositions x were also determined. The optical constants (the refractive index n, the absorption index k, the absorption coefficient t, the dielectric constants $\varepsilon_1$ and $\varepsilon_2$) of SnTe$_x$Se$_{1-x}$ films were determined for different thickness in the spectral range 500-2500 nm. The optical absorption results indicate that, the fundamental absorption edge for SnTe$_x$Se$_{1-x}$ (0≤x≤0.6) films is due to an allowed, direct and indirect transition energy gaps and only direct energy gap for 0.8≤x≤1. It was found that, the optical energy gaps for annealed films decreased as compared with the as-deposited films. This decrease of the energy gaps is attributed to the change in the structure of the films from amorphous to crystalline. The variations of the optical constants (n, k, $\varepsilon_1$ and $\varepsilon_2$) with composition were investigated.

1 Introduction

The investigations of IV-VI semiconductors have been going on for many years. The semiconducting compounds from the group A$^2$B$^3$ form a continuous series of solid solutions with NaCl structure. This system is a promising material for opto-electronics in the far-infrared region of the spectrum and for thermoelectric transducers at medium high temperature. Recently, attention has been focused on the physical properties of layered tin mono-chalcogenide semiconductors (SnSe, SnS and SnTe) because of their use in holographic recording systems, infrared detectors, and switching devices and as an efficient solar cell material.

A number of attempts have been made by different workers to investigate the electrical and optical properties of SnSe, SnS and SnTe thin films. The solid solutions SnTe$_x$Se$_{1-x}$, (0≤x≤1) display some peculiarities in the band structure and properties that make them an interesting object for both applied and fundamental physical research.

Among the outstanding features of SnTe$_x$Se$_{1-x}$ with (0≤x≤1) alloy, the continuous variation of energy band gap and lattice constants, as well as the optical properties with the variation of the constituent compounds is of particular importance. The aim of this work is to study the structural properties and to investigate the optical properties of the ternary alloy of the composition SnTe$_x$Se$_{1-x}$ with (0≤x≤1) in the form of thin films and to determine the variation in its physical properties with composition and temperature over a wide range.

2 Experimental Details

The semiconductor alloys SnTe$_x$Se$_{1-x}$, (0≤x≤1) were prepared by fusion method. In this method, Sn, Te and Se in stoichiometric proportion (with an accuracy of 5×10$^{-3}$g/m) were sealed into evacuated and graphitized silica tubes at a pressure of about 10$^{-3}$ torr. The temperature of the tubes was gradually raised in an automatically-controlled furnace, up to 1150 K, and then kept for nearly 50 hrs at this temperature to allow Sn, Te and Se to react completely with continuous vibrational shaking to
ensure homogeneity of the sample. The tubes were gradually cooled with a cooling rate of about 25 °C/h to room temperature in order to obtain polycrystalline SnTe,Se, compounds. The films were prepared by thermal evaporation from a molybdenum boat under the bell of a vacuum system of type Lybold Heraeus Univex-300. Evaporation and deposition of films took place under vacuum of 10⁻³ torr, on clean glass substrates at 300 K. The rate of deposition was estimated at about 30 nm/min and the substrates were rotated, during the deposition process, to ensure homogeneity. The film thickness (ranging between 170 and 200 nm) was measured using interferometric techniques.

Fig. 1 — X-ray diffraction pattern for SnTe₀.₆Se₀.₄ thin films

Fig. 2 — X-ray diffraction pattern for SnTe₀.₆Se₀.₄ thin films

Fig. 3 — Spectral distribution of T and R for SnTe₀.₆Se₀.₄ thin films annealed at 423 K and as-deposited

Fig. 4 — Absorption coefficient square α² versus photon energy hν for SnTe₀.₆Se₀.₄ thin films of different thickness
Fig. 5 — Spectral distribution of \( T \) and \( R \) for \( \text{SnTe}_x\text{Se}_{1-x} \) thin films \((0 \leq x \leq 1)\) annealed at 423 K.

Table 1 — Calculated lattice parameter values for \( \text{SnTe}_x\text{Se}_{1-x} \) alloy \((0 \leq x \leq 1)\) system

<table>
<thead>
<tr>
<th>Composition</th>
<th>System: Orthorhombic Cubic</th>
<th>Lattice parameters</th>
<th>Lattice parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( a(\text{Å}) )</td>
<td>( b(\text{Å}) )</td>
</tr>
<tr>
<td>0.0</td>
<td></td>
<td>11.44</td>
<td>4.10</td>
</tr>
<tr>
<td>0.2</td>
<td></td>
<td>11.56</td>
<td>4.20</td>
</tr>
<tr>
<td>0.4</td>
<td></td>
<td>11.60</td>
<td>4.22</td>
</tr>
<tr>
<td>0.6</td>
<td></td>
<td></td>
<td>6.23</td>
</tr>
<tr>
<td>0.8</td>
<td></td>
<td></td>
<td>6.25</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>6.30</td>
</tr>
</tbody>
</table>

3 Results and Discussion

3.1 Structural investigation

The crystal structure and composition of \( \text{SnTe}_x\text{Se}_{1-x} \) alloy \((0 \leq x \leq 1)\) in both powder and thin film forms were examined by X-ray diffractometer (Philips PW1373) and an electron probe microanalysis (EMPA) using X-ray wavelength dispersive spectroscopy (WDS).

From X-ray powder diffraction patterns of the prepared \( \text{SnTe}_x\text{Se}_{1-x} \), where \( x = 0, 0.2, 0.4, 0.6 \) and 0.8, the positions and heights of the peaks were calculated and compared with the standard (JCPDS) international centre for diffraction data 1996 cards for the SnSe and SnTe. These results showed that, the prepared \( \text{SnTe}_x\text{Se}_{1-x} \) bulk had a single cubic structure for \( \text{SnTe}_x\text{Se}_{1-x} \) and \( \text{SnTe}_{0.6}\text{Se}_{0.4} \), and orthorhombic crystal structure for \( \text{SnTe}_{0.8}\text{Se}_{0.2} \) and \( \text{SnSe} \).

Fig. 6 — Plot of \( \alpha \) versus \( h^2 \) for \( \text{SnTe}_x\text{Se}_{1-x} \) thin films annealed at 423 K.

Fig. 1 shows X-ray diffraction patterns for \( \text{SnTe}_x\text{Se}_{1-x} \) for bulk and the as-deposited and annealed thin films as a representative example for cubic structure. Fig. 2 shows the crystal structure for \( \text{SnTe}_x\text{Se}_{1-x} \) for bulk and the as-deposited and annealed thin films as a representative example for the orthorhombic crystal structure. The calculated lattice parameter values for \( \text{SnTe}_x\text{Se}_{1-x} \) alloy \((0 \leq x \leq 1)\) system whether of the cubic or orthorhombic structural powder form are listed in Table 1. It was found that, the calculated lattice parameters are in good agreement with the reported values\(^{8,10,14}\) for \( x = 0, 0.2, 0.4, 0.6, 0.8 \) and 1.

Moreover, X-ray studies showed that, all the as-deposited films of \( \text{SnTe}_x\text{Se}_{1-x} \) \((0 \leq x \leq 1)\) have amorphous structure. After annealing for one hour at 423 K, under vacuum of \( 10^{-4} \) torr, these films change to crystalline form as shown in Figs 1 and 2.
Table 2 — Compositional analysis of the powder and amorphous thin films of SnTe,Se system

<table>
<thead>
<tr>
<th>Starting compositions</th>
<th>Concentration of the powder</th>
<th>Following elements amorphous films</th>
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<tbody>
<tr>
<td></td>
<td>Sn</td>
<td>Te</td>
</tr>
<tr>
<td>SnSe</td>
<td>49.658</td>
<td>—</td>
</tr>
<tr>
<td>SnTe_{x}Se_{1-x}</td>
<td>50.844</td>
<td>9.933</td>
</tr>
<tr>
<td>SnTe_{x}Se_{1-x}</td>
<td>49.776</td>
<td>20.842</td>
</tr>
<tr>
<td>SnTe_{x}Se_{1-x}</td>
<td>50.6021</td>
<td>29.9535</td>
</tr>
<tr>
<td>SnTe_{x}Se_{1-x}</td>
<td>50.2753</td>
<td>40.3334</td>
</tr>
<tr>
<td>SnTe</td>
<td>49.8418</td>
<td>50.1582</td>
</tr>
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</table>

Table 3 — The previously reported results of the direct and indirect energy gaps of the as-deposited SnSe and SnTe thin films together with our results for the as-deposited and annealed films for comparison

<table>
<thead>
<tr>
<th>Thin films</th>
<th>Author</th>
<th>No. of Ref.</th>
<th>$E_g^d$ (eV)</th>
<th>$E_g^a$ (eV)</th>
<th>$E_g^d$ (eV)</th>
<th>$E_g^a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnSe</td>
<td>Dang (1987)</td>
<td>32</td>
<td>1.19</td>
<td>0.95</td>
<td>1.12</td>
<td>0.835</td>
</tr>
<tr>
<td>SnSe</td>
<td>John (1994)</td>
<td>14</td>
<td>1.195</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>SnSe</td>
<td>Singh (1991)</td>
<td>3</td>
<td>1.12</td>
<td>0.94</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>SnSe</td>
<td>Dang (1984)</td>
<td>29</td>
<td>1.21+0.02</td>
<td>0.96+0.025</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>SnTe</td>
<td>Present work</td>
<td>as deduced 12</td>
<td>0.18</td>
<td>0.16</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>SnTe</td>
<td>Fouad (1994)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

The diffractograms of the annealed thin films indicate a preferred orientation of the films along 400 for films with $x = 0, 0.2$ and $0.4$ as shown in Fig. 2 as a representative example of $x = 0.4$. For thin films with $x = 0.6, 0.8$ and $1$ the diffractograms of the annealed films indicate a preferential orientation of the films along 200, as a representative example for $x = 0.6$ (Fig. 1).

X-ray diffraction patterns of both the powder and the corresponding annealed thin films of different compositions (SnTe, SnTe_{0.2}Se_{0.8}, SnTe_{0.1}Se_{0.9}, SnTe_{0.5}Se_{0.5}, SnTe_{0.3}Se_{0.7}, SnTe_{0.2}Se_{0.8} and SnSe) confirm that, the composition of each was not perturbed during evaporation. The composition of the powder and the thin film samples for SnTeSe_{1-x} (0 ≤ x ≤ 1) system was determined by electron microprobe analysis, with accuracy better than 2%. The results of the compositional analysis are reported in Table 2. It was found that, these results confirm the results obtained from X-ray analysis.

3.2 Optical properties

Analysis of the optical absorption spectra is one of the most accurate methods for determination of optical constants [the refractive index $n$, the absorption index $k$, the absorption coefficient $\alpha$ and the optical energy gap $E_g$] and understanding the type of transition across the forbidden energy gap and developing the band structure of semiconductors.

Effect of annealing and thickness on the optical properties of SnTeSe_{1-x} (0 ≤ x ≤ 1) thin films — The transmittance $T$ and reflectance $R$ of SnTeSe_{1-x} (0 ≤ x ≤ 1) thin films were measured at normal incidence using a UV-VIS-NIR spectrophotometer Shimadzu in the spectral range 500-2500 nm.

The transmission $T$ is given by:

$$T = \frac{[1-R]^2 \exp (-\alpha t)]}{[1-R' \exp (-2 \alpha t)]}$$

(1)
where $\alpha = 4 \pi k/\lambda$ is the absorption coefficient and $k$ is the extinction coefficient.

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad \ldots \quad (2)$$

The real and imaginary parts $\varepsilon_1$ and $\varepsilon_2$ of the complex dielectric constants can be determined:

$$\varepsilon_1 = n^2 - k^2 \quad \text{and} \quad \varepsilon_2 = 2 n k \quad \ldots \quad (3)$$

This curve showed that, both fresh and annealed samples show a similar trend, but annealing at 423 K for one hour changes the values of both $R$ and $T$ by about 8%. Fig. 4 represents the relation between the absorption coefficient $\alpha^2$ versus photon energy $\hbar \gamma$ for SnTe$_{0.5}$Se$_{0.5}$ thin films of different thickness as a representative example and also the inset of this figure gives the variation of the direct energy gap $E_g^d$ with the thickness. From Fig. 4 it is clear that the dependence of the optical energy gap on thickness greater than 1700Å (1700-1800 Å) and annealed at 423K for one hour, as the thickness has negligible effect on the optical properties.

**Compositional dependence of the optical constants of SnTe$_x$Se$_{1-x}$ ($0 \leq x \leq 1$)** — Fig. 5 represents the spectral distribution of both transmission $T$ and
reflection $R$, at nearly normal incidence in the spectral range 500-2500 nm for SnTe$_x$Se$_{1-x}$ thin films of different compositions $x = 0-0.8$ and of thickness around 1750 Å annealed at 423 K for one hour. From Fig. 5, it is clear that, all transmission absorption coefficient data were analyzed in terms of the relation\(^{15,16}\):

$$\alpha = \text{constant } h\gamma - E_g^p$$  \(\text{(4)}\)

where $p$ determines the type of transition, being 1/2 for allowed direct transition, 3/2 for forbidden direct transition, 2 for indirect, allowed, transition and 3 for forbidden, indirect, transition.

and reflection data of the different composition have the same trend. Fig. 6 shows the variation of the calculated absorption coefficient $\alpha$ at different photon energies $h\gamma$ for different compositions of SnTe$_x$Se$_{1-x}$ (0$\leq x \leq$1) annealed thin films. The absorption coefficient data were analyzed in terms of the relation\(^{15,16}\):

$$\alpha = \text{constant } h\gamma - E_g^p$$  \(\text{(4)}\)

where $p$ determines the type of transition, being 1/2 for allowed direct transition, 3/2 for forbidden direct transition, 2 for indirect, allowed, transition and 3 for forbidden, indirect, transition.

Fig. 10 — Dispersion curves of $\eta, k$ for SnTe$_x$Se$_{1-x}$ thin films annealed at 423 K

The curves in Fig. 6 exhibit the following feature:

I. The values obtained for $\alpha$ were fairly high $\alpha = 10^4-2\times10^5$ cm$^{-1}$ as most high carrier concentration semiconductors and the absorption increases with increasing photon energy.

II. In high $h\gamma$ ranges the plots of the different composition SnTe$_x$Se$_{1-x}$ (0$\leq x \leq$1) thin films are linear and can be described by Eq. (4) with $p = 2$ which corresponds to indirect, allowed, transition.

Fig. 11 — Dispersion curves of dielectric constants $\varepsilon_1$ and $\varepsilon_2$ for SnTe$_x$Se$_{1-x}$ thin films annealed at 423 K

The curves in Fig. 6 exhibit the following feature:

I. The values obtained for $\alpha$ were fairly high $\alpha = 10^4-2\times10^5$ cm$^{-1}$ as most high carrier concentration semiconductors and the absorption increases with increasing photon energy.

II. In high $h\gamma$ ranges the plots of the different composition SnTe$_x$Se$_{1-x}$ (0$\leq x \leq$1) thin films are linear and can be described by Eq. (4) with $p = 2$ which corresponds to indirect, allowed, transition.
The first term represents the contribution of phonon absorption and must be zero if $h \gamma < E_v - E_p$ while the second term corresponds to phonon emission and is to be zero if $h \gamma < E_v + E_p$.

Fig. 9 shows the dependence of $(a h \gamma)^{1/2}$ versus $h \gamma$ for four different compositions SnTe$_{0.1}S_{0.9}$, SnTe$_{0.5}S_{0.5}$, SnTe$_{0.4}S_{0.6}$ and SnSe. It is clear that, these curves are approximately close to two straight lines:

The line for low value of $(a h \gamma)^{1/2}$ corresponds to transition with absorption of photon $h \gamma = E_v - E_p$. Its extrapolation cuts the $h \gamma$ axis at $E_v - E_p$: The line for the high values of $(a h \gamma)^{1/2}$ corresponds to transition with emission of photon $h \gamma = E_v + E_p$. Its extrapolation cuts the $h \gamma$ axis at $E_v + E_p$.

The indirect energy gap $E_v$ as well as the photon energy $E_p$ can be obtained from these intercepts as:

$$E_v = 1/2 (h \gamma_{1} + h \gamma_{2}), E_p = 1/2 (h \gamma_{1} - h \gamma_{2})$$

Fig. 8 shows the dependence of both $E_v$ and $E_p$ with composition for the as-deposited thin films which is of the same trend, namely that, as $x$ increases $E_v$ and $E_p$ decreases reaching zero for $x > 0.6$. Table 4 shows the value of the absorbed or emitted photon energy $E_p$ for the different values of $x$. In the indirect transitions, the value of the absorbed or emitted photon energy depends on the value of $x$; it decreases as $x$ increases for the annealed films. To our knowledge, no indirect gap was previously reported except by Singh and Dag, for as-deposited SnSe films only, which are very close to our data and lower than the annealed one.

Figs 10 and 11 show the variation of the optical constants $n$, $k$ and the dielectric constants $\varepsilon_r$ and $\varepsilon_s$ with photon energy $h \gamma$ for SnTe,Se$_{1-x}$, thin films with different compositions. It is clear from these curves that, the general behaviour of these constants is the same. These curves show sharp increase at low energy range and then increase slightly in the high-energy range tending to be constant at very high energy.

4 Conclusion

The structural and optical properties of the ternary alloys SnTe,Se$_{1-x}$, $(0 \leq x \leq 1)$, prepared by fusion method have been carefully studied. Thin
films of these alloys were obtained by thermal evaporation on glass substrates. It has been demonstrated that the obtained SnTe,Se_{1-x} (0\leq x \leq 1) films were amorphous in structure, at room temperature, and by heat treatment under vacuum of 10^{-3} torr for one hour at 423 K became crystalline. X-ray analysis measurements show that, SnTe,Se_{1-x} alloys have orthorhombic and cubic structure, depending on the value of x.

The optical absorption spectra of evaporated films of the different compositions of the non-stoichiometric SnTe,Se_{1-x} (0\leq x \leq 1) have been measured. Experimental evidence for the semiconductor nature of both as-deposited and annealed SnTe,Se_{1-x} (0\leq x \leq 1) films includes the following:

High absorption coefficient \alpha \sim 10^4 as most semiconductors; the shape of the optical absorption spectra is that of a semiconductor in the region of the fundamental absorption; Also the optical absorption spectra revealed the existence of direct and indirect energy gaps for SnTe,Se_{1-x} (0\leq x \leq 0.6) and direct energy gap only for x (0.8\leq x \leq 1). The present data of dependence of both direct and indirect energy gaps on x show a decrease in both direct and indirect energy gaps with increasing x. The general behaviour of n, k, \varepsilon_1, and \varepsilon_2 was almost the same, since they increased by increasing the photon energy. At a given wavelength, n, k, \varepsilon_1, and \varepsilon_2 were found to increase with increasing x. Also, it was found that, both direct and indirect energy gaps decreased for the annealed films as compared with the as-deposited films. At a given wavelength, n, k, \varepsilon_1, and \varepsilon_2 decreased for the annealed films.

References