Effect of Composition on The Structural, Morphology, and Optical Properties of AgSb(SxSe1-x)2 Thin Films

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Abstract: Quenching method was used to prepare alloys of the AgSb(SxSe1-x)2 quaternary compound with different sulfur content. AgSb(SxSe1-x)2 thin films with different sulfur concentration were prepared at room temperature 303K on glass substrate using pulsed laser deposition under vacuum of 10^-2 bar, thickness of ~100nm. The structure of the prepared alloys and thin films were examined by x-ray diffraction. The results declared that all the prepared compounds have polycrystalline with cubic structure whereas the deposited AgSb(SxSe1-x)2 thin films were amorphous. Atomic Force Microscopy revealed that the average grain size decreases while roughness exhibit to increase in non-regular manner with the increase of sulfur concentration. The absorbance and the transmittance were provided from visible spectrophotometer measurements in the wavelength range (300-1100nm). The results showed that the prepared thin films have indirect allowed band gap which showed absorbable increase with the increase of sulphur content, indeed the optical energy gap increase from 1.1 to 1.7 eV with the increase of sulphur content while all the optical constants (the refractive index n, the extinction coefficient k and real and imaginary parts of dielectric constants εr, εi all declared reduction with the increase of sulfur concentration.

1 Introduction
AgSbSe2 and AgSbTe2 ternary chalcogenides which classify as semiconductors compound with disordered NaCl cubic structure whereas silver and antimony occupy metal sub lattice [1]. Both compounds have been have received much attention in recent years, partly because of their interesting fundamental properties and partly because of their many potential applications in optical imaging, optical recording, infrared optics, and more recently, optical communications [1-8]. This research concened on the investigation on the influence of sulfur content on the structural, morphology and optical parameters like optical energy gap, optical constants of the AgSb(SxSe1-x)2 thin films prepared pulsed laser deposition technique.
2 Experimental details

Appropriate amounts of pure elements (silver, tin, selenium, and sulfur) provided from Fluca, Germany are weighed according to their atomic weight ratio and put in an ampoule made of quartz (length ~ 25 cm and internal diameter ~ 8 mm) materials are evacuated to (~10⁻⁵ Torr) and sealed, and then heated at 1273 K for 5 hours and then left to cool to room temperature. Glass slides substrates were used which were subjected to several steps to remove any contamination such as dust, oily material, grease, and some oxides using soap solution, then the glass slides were placed in a clean beaker containing distilled water and with ethanol solution then the glass slides were dried by blowing air. Thin films were prepared using pulsed lasered deposition method under vacuum of (~10⁻³ Torr). The deposition was done by focusing Nd: YAG (Huafei Tongda Technology - Diamond-288 pattern EPLS) Q-switching laser beam which coming from a window is incident on the target surface making an angle of 45° with it. The characteristics of the laser tool were (1) Laser model: Q-switched Nd: YAG Laser, Second Harmonic Generation (SHG), Laser wavelength: (1064 / 532) nm, (2) Pulse energy: (100-1000) mJ, (3) Pulse width: 10ns, (4) Repetition frequency: (1, 2, 3, 4, 5, 6) Hz, (5) Cooling method: inner circulation water cooling, and (6) Applied voltage: 220V. The substrate is placed in front of the target with its surface parallel to that of the target. Sufficient gap is kept between the target and the substrate so that the substrate holder does not obstruct the incident laser beam. X-ray diffraction (XRD) was used to check the structures of the prepared alloys and thin films. The present work used an X-ray diffractometer type (Miniflex II), with Cu-Kα x-ray tube (λ = 1.54056 Å) is used. The morphology is obtained using atomic force microscopy AFM. UV/Visible spectrophotometer type SP-8001 was used to study the optical properties of AgSb(SₓSe₁−x)₂ films in the wavelength range 200-1100 nm. This spectrometer contains two light sources Deuterium and Tungsten lamp within the wavelengths range 190–390 nm and 390–1100 nm of the spectrum respectively. The obtained transmittance and absorbance as function of wavelength are used to estimate the optical energy gap and the optical constants like refractive index (n), extinction coefficient (k) and real and imaginary parts of dielectric constants(ε_r, ε_i) using the following relation respectively:

The complex refractive index (n_c) is defined as [9]:

\[ n_c = n - ik \]

And it is related to the velocity of propagation (v), and light velocity (c) by:

\[ v = \frac{c}{n_c} \]

The refractive index value can be calculated from the formula [9]:

\[ n = \sqrt{\frac{4R}{(R-1)^2 - k^2}} \left( \frac{R+1}{R-1} \right) \]

Where R is the reflectance, and can be expressed by the relation [10]:

\[ R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \]

The extinction coefficient, which is related to the exponential decay of the wave as it passes through the medium, is defined as [6]:

\[ k = \frac{\alpha \lambda}{4\pi} \]

Where \( \lambda \) is the wavelength of the incident radiation and \( \alpha \) is given by [9]:

\[ \alpha = 2.303 \frac{A}{t} \]
(n−ik)² = ε, −iε ........................................... (7)

Where

εi = n² − k² ........................................... (8)

And ε = 2nk ........................................... (9)

3 Results and Discussion

The main purpose of this section is to investigate the structural type of semiconductor material that is relevant to the work and to ensure that the structure will not be changed after evaporation. Also, the influence of sulfur content on the structure of the prepared thin films has been investigated. The x-ray diffraction spectrum of AgSb(SxSe1-x)2 alloys with different sulfur content is shown in Figure 1. From the figure, it is clear that the main diffraction peaks indexed by (111), (200) and (220) are related to the cubic structure of AgSb(SxSe1-x)2 as pointed out by previous studies as well as the diffraction peaks identified as orthorhombic AgSbSe2 phase (PDF 96-901-1029) and Ag5SbS4 phase (PDF 96-900-7511) as marked in the figure. It is obvious the increment of composition ratio resulted in the reduction of these quaternary dominant peaks intensities as seen in same Figure. The grain size was found to increase in the first and then decreases with further increase of sulfur content. These results are coinciding with Vela et al [12]. The interesting result in the work the diffraction pattern are absent from the present of any other phases of Ag-Sb-S-Se system.

Figure 1: X-ray diffraction of AgSb(SxSe1-x)2 compounds alloys with different sulfur content.

Figure 2 show the X-ray diffraction patterns for AgSb(SxSe1-x)2 films for different sulfur content (x= 0.2,0.4,0.8,and 1.0 ), these patterns show that all films have amorphous structures, since all the patterns are absent from any diffraction peaks, these results are in agreement with Frumar and Wagner.
[13], the amorphous structure related with low thickness of the prepared samples thin films, the
structure may be turn to poly crystalline with increase of thickness.

Figure 2: X-ray diffraction of AgSb(S_xSe_{1-x})_2 thin films with different sulfur content.

3.1 Atomic Force Microscopy Analysis (AFM)
Atomic force microscopy technique was subjected to measure the grain size and average roughness of
as well as the surface morphology AgSb(S_xSe_{1-x})_2 thin films with different sulfur content(0.2, 0.4, 0.8, and 1.0 prepared by pulsed laser deposition. Figure.3 shows their surface morphologies analyzed by AFM. The measured grain size and RMS roughness are listed in Table.1. It is obvious that the average grain size exhibit to change in reverse manner with the increase of sulfur content i.e. The average grain size get to reduce with the increase of sulfur content, indeed average grain size decreases from 81.34 to 64.07 nm when sulfur content increases from 0.2 to 1.0. The roughness of the films shows nonsystematic variation with the increase of sulfur concentration, moreover the values of surface roughness were found to increase from 0.857 to 0.951 nm with increase of sulfur from 0.2 to 0.4 and then decrease to 0.675 nm with further increase of sulfur concentration.

Table 1 Average grain size and average roughness for AgSb(S_xSe_{1-x})_2 films with different sulfur content.

| x   | Average roughness (nm) | Average grain size (nm) |
|-----|------------------------|-------------------------|
| 0.2 | 0.857                  | 81.34                   |
| 0.4 | 0.951                  | 79.09                   |
| 0.8 | 0.250                  | 75.40                   |
3.2 The Optical Properties of AgSb(S_xSe_{1-x})_2 Films

The optical properties of the AgSb(S_xSe_{1-x})_2 thin films on glass for at room temperature with different sulfur concentration (0.2, 0.4, 0.8 and 1.0) nm have been determined using UV-visible spectrophotometer in the region (300–1100) nm. The optical parameters were determined using the absorbance and transmittance. The absorbance spectra of the prepared AgSb(S_xSe_{1-x})_2 thin films with different composition was plotted in Figure 4. In general, one can observe from Figure 4 that absorbance decreases with increasing of sulfur concentration which means an increase of transmittance also means that addition of sulfur make AgSb(S_xSe_{1-x})_2 thin films more transparent or less opaque to the wavelength. The shifts of absorbance toward shorter wavelength (higher energies) accompanied the increment of sulfur content is related with reduction of grain size, the reduction of grain size increases the lattice parameters and hence wide the energy gap.
3.3 The Optical Energy Gap

The variation of \((\alpha h\nu)^{1/2}\) versus the photon energy \((h\nu)\) is plotted in figure 5. The optical energy gap values \(E_{g}^{\text{opt}}\) for AgSb(S\(_{x}\)Se\(_{1-x}\))\(_{2}\) thin films have been determined by extrapolation i.e. \(E_{g}^{\text{opt}}\), of the portion at \([(\alpha h\nu)^{1/2} = 0]\). It is found that the relation for \(r = 2\) for allowed indirect transition yields linear dependence. The value of the optical energy gap reveals an increase with the increase of sulfur concentration; moreover \(E_{g}^{\text{opt}}\) increases from 1.10eV to 1.70eV when sulfur concentration increases from 0.2 to 1.0, although \(E_{g}^{\text{opt}}\) exhibit to decreases as sulfur concentration increased from 0.2 to 0. 4 , this is can be explained as follows ,It is well know that \(E_{g}^{\text{opt}}\) value of sulfur element is wide than selenium element , thus the increase of sulfur concentration in the film samples on the expense of selenium concentration lead to an increase of optical energy gap. On the other hand the direct energy gap were estimated throughout plotting the diagram between the variation of \((\alpha h\nu)^{2}\) versus the energy of the incident photon as shown in Figure.6 and the values are listed in table 3. It is obvious that direct \(E_{g}^{\text{opt}}\) variation of direct \(E_{g}^{\text{opt}}\) have the same trend of that of indirect one, indeed it is found that \(E_{g}^{\text{opt}}\) decreased as x increased from 0. 2 to 0.4 but then \(E_{g}^{\text{opt}}\) increased from 2.2 to 2.6 eV with the increase of sulfur concentration in from 0.4 to 1.0.

Figure 4: The absorbance spectrum of AgSb(S\(_{x}\)Se\(_{1-x}\))\(_{2}\) thin films with different sulfur content.

Figure 5: The plot diagram between \((\alpha h\nu)^{1/2}\) versus \((h\nu)\) of AgSb(S\(_{x}\)Se\(_{1-x}\))\(_{2}\) thin films with different sulfur content.
Figure 6: The plot diagram between \((\alpha h\nu)^2\) versus \(h\nu\) of \(\text{AgSb(S_xSe_{1-x})_2}\) thin films with different sulfur content.

The wavelength dependence of the refractive index in the range 300-1100nm, of \(\text{AgSb(S_xSe_{1-x})_2}\) thin films with different sulfur content (0.2, 0.4, 0.8, and 1.0) prepared at R.T is shown in Figure 7. It is clear from this figure and Table 3 that the refractive index, get to reduce with the increase of sulfur concentration in the prepared samples, moreover, \(n\) decreases from 4.512 to 2.896 for \(\text{AgSb(S_xSe_{1-x})_2}\) films when \(x\) increases from 0.2 to 1.0, this behavior can be explained on the basic of that increasing of sulfur make the sample more transparent also the increase of sulfur decreases the packing density of \(\text{AgSb(S_xSe_{1-x})_2}\) or make the sample less dense which in turn increases the propagation velocity of light through them which resulting in reducing the refractive index values since \(n\) represent the ratio of light velocity through vacuum to velocity through any medium.

Figure 7: Wavelength dependence of the refractive index of \(\text{AgSb(S_xSe_{1-x})_2}\) thin films with different sulfur content.
Figure 8 showed the variation manner of the extinction coefficient of AgSb (S_xSe_{1-x})_2 films with different sulfur content. The results showed that the extinction coefficient decreases with the increase of sulfur concentration. It is clear that for as deposited AgSb(S_xSe_{1-x})_2 films k decreases from 0.448 to 0.077 when x increases from 0.2 to 1.0, the behavior explanation is the increase of sulfur make the sample more transparent and hence decreased the absorption coefficient decreases consequently k will be reduces.

![Figure 8: Wavelength dependence of the extinction coefficient k of AgSb(S_xSe_{1-x})_2 thin films with sulfur content.](image)

The relation between the real ($\varepsilon_r$) and imaginary ($\varepsilon_i$) parts of the dielectric constant values and wavelength in the range (300–1100)μm of AgSb(S_xSe_{1-x})_2 films deposited at R.T with different composition(x=0.2,0.4,0.8, and 1.0) are shown in Figures (9 and 10). The variation trend of $\varepsilon_r$ is similar to that of the refractive index because of the smaller value of $k^2$ compared with $n^2$ according to equation (7), while $\varepsilon_i$ exhibit to change in similar manner to that of k. It is found that $\varepsilon_r$ decreases with the increase of sulfur addition, moreover $\varepsilon_r$ found to increase from 20.155 to 8.381 for thin films deposited at R.T when sulfur concentration increases from 0.2 to 1.0 as shown in Table.3. The imaginary part of dielectric constant $\varepsilon_i$ reveal the same behavior of $\varepsilon_r$ with x content. It is clear from Table.3 that $\varepsilon_i$ for AgSb(S_xSe_{1-x})_2 films decreases from 4.044 to 0.446 when sulfur concentration increases from 0.2 to 1.0. The same explanation of n and k can be given to $\varepsilon_r$ and $\varepsilon_i$.

![Figure 9: Wavelength dependence of $\varepsilon_r$ of AgSb(S_xSe_{1-x})_2 thin films with different sulfur content.](image)
Figure 10: Wavelength dependence of $\varepsilon_i$ with wavelength of AgSb(S$_x$Se$_{1-x}$)$_2$ thin films with different sulfur content.

Table 2: Values of $E_g^{opt}$ and Optical constants at $\lambda=700$ nm for AgSb(S$_x$Se$_{1-x}$)$_2$ thin films with different sulfur content.

| Sample | T%  | $\alpha$ (cm$^{-1}$) | k    | n    | $\varepsilon_r$ | $\varepsilon_i$ | $E_g$ (eV) | $E_g$ (eV) |
|--------|-----|----------------------|------|------|-----------------|-----------------|-----------|-----------|
| 0.2    | 10.53 | 112571               | 0.448| 4.512| 20.155          | 4.044           | 1.10      | 2.32      |
| 0.4    | 11.40 | 108586               | 0.432| 4.615| 21.114          | 3.990           | 1.05      | 2.20      |
| 0.8    | 53.70 | 31091                | 0.124| 3.681| 13.534          | 0.911           | 1.55      | 2.5       |
| 1.0    | 67.92 | 19345                | 0.077| 2.896| 8.381           | 0.446           | 1.70      | 2.6       |

4 Conclusions

1- Pulsed laser deposition provided thin films from AgSb(S$_x$Se$_{1-x}$)$_2$ with amorphous structure for all sulfur content.

2- The increase of sulfur content result in nonsystematic change of the grain size.

3- The increasing of sulfur concentration lead to proceeding reduction of the absorbance for the prepared thin films.

4- The prepared thin films showed indirect and direct allowed transition and the band gap decreases with the increase of sulfur concentration in the first but then optical energy gap increased with further increase of sulfur concentration leading to shifting the absorption edge to higher energies.

5- The rule of sulfur concentration become more pronounced for $x>0.4$.

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