Structural and Optical Constants of Annealed As\textsubscript{47.5}Se\textsubscript{47.5}Ag\textsubscript{5} Film using DSC Transformation Curve

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The effect of thermal annealing process on both structural and optical properties of amorphous As\textsubscript{47.5}Se\textsubscript{47.5}Ag\textsubscript{5} thin films was studied. The X-ray diffraction studies exhibit that the crystallinity was improved by increasing the annealing temperature. Further, the crystallite size and the crystallinity increase whereas dislocation density and strain decrease with increase of annealing temperatures. The optical constants of the as-prepared and annealed of As\textsubscript{47.5}Se\textsubscript{47.5}Ag\textsubscript{5} thin films were calculated using envelope method. The optical absorption data in these films were successfully describes by Tauc’s relation which exhibit the indirect transitions for as-prepared sample and allowed direct transition for annealed sample above onset temperature \(T_c\). It is evident that the energy gap \(E_g\) decreases and the localized states \(E_l\) increases as a function annealing temperature. The dispersion of the refractive index \(n\) for these films was discussed using the single oscillator model proposed by the Wemple–DiDomenico relationship.

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1. Introduction

Chalcogenide glasses are formed from group VI elements (S, Se, and Te) of the periodic table. Glassy alloys containing chalcogen elements were initially studied for their interesting semiconducting properties and more recent applications in reversible phase-change optical recording, memory switching and optical data storage [1, 2]. Thermal annealing is an important method for investigation of the reduction of the intrinsic defects in amorphous state and study the transition from amorphous state to crystalline state of the same materials for using switching electrical and optical devices [1–6].

Furthermore, the amorphous-crystalline semiconductors materials based on Se, Te, and S have a high third order non-linearity and are often alloyed with Ge, Sb, or As in order that obtain higher sensitivity and crystallization temperature as well as ageing effects, so in order to beat these problems the As, Se, and As\textsubscript{5}Se\textsubscript{3} are considered among the most studied binary systems [7–9]. Otherwise, addition Ag atom on chalcogenide glasses exhibit a peculiar characteristic of mixed ionic-electronic conductors, which provide dynamical ion movement by electron excitation.

Also, lead to develop the glass forming area and create compositional and configurational disorder in the system and has large effect on their structural, physical and thermal properties, thus are considered as candidate materials in batteries, optics, optoelectronics, chemistry, and biology [3, 10–16]. Generally, the non-linear refractive index of chalcogenide glasses of Ag-doped is higher than that of the un-doped glasses because the presence of silver (transition-metal) atoms formed easily polarizable electron clouds is a evident advantage [14]. Optical properties of the Ag doped As–Se chalcogenide thick films have been determined with high precision for optoelectronics applications have been reported our previous work [3].

In the present work, the effect of thermal annealing process on both the structural and optical properties of amorphous As\textsubscript{47.5}Se\textsubscript{47.5}Ag\textsubscript{5} chalcogenide thin film was investigated. X-ray diffraction pattern has been carried out to follow the structural changes resulting from heat treatment of the as-prepared films at different temperatures. Also, the effect of structural transformations on their optical properties was also investigated.

2. Experimental procedures

2.1. Preparation of the bulk material

Bulk sample of As–Se–Ag was prepared using melt quenching technique from mixing of As, Se, and Ag elements with purity 99.999% (Aldrich ChemCo, USA). Ac-
According to their atomic percentage the stoichiometric ratios were shut-in a quartz glass ampoule under a vacuum of $10^{-5}$ Torr. Through the heating process the ampoule must be frequently rocked to ensure the homogeneity of molten materials. After achieving the desired time, the ampoule containing the molten materials were rapidly quenched in a mixture of ice and water to get the bulk glass of As–Se–Ag [17]. The crystallization kinetics of $\text{As}_{47.5}\text{Se}_{47.5}\text{Ag}_{5}$ glass was investigated using a Shimadzu 50 differential scanning calorimeter (DSC) with an accuracy of $\pm 0.1$ K. More details are shown in Ref. [17].

2.2. Preparation of the thin films

Thin films of As–Se–Ag sample were prepared by thermal evaporation technique using a coating unit (DV-502A; Denton Vacuum, Cherry Hill, NJ, USA) under high vacuum conditions ($10^{-7}$ mbar). The substrates utilized for deposition were carefully cleaned using ultrasonic hot bath distilled water and pure alcohol before the evaporation process started [3]. The structure and phase of the as-deposited films and annealed films in a vacuum of ($10^{-3}$ mbar) with five different temperatures 463, 532, 604, 613, and 623 K, respectively, for a fixed time (30 min) and then cooled down to room temperature. The annealed thin films were examined using a Philips 1710 X-ray diffractometer (XRD). The transmittance and reflectance spectra for as-deposited and annealed films were obtained by a double-beam computer-controlled spectrophotometer (UV-2101, Shimadzu) at normal light incidence in the range of wavelength from 400 to 2500 nm.

3. Results and discussion

3.1. Structural characterization

The DSC curves for the as-prepared $\text{As}_{47.5}\text{Se}_{47.5}\text{Ag}_{5}$ glass at heating rate 20 K/min shown in Fig. 1. One can have observed three characteristic phenomena are clear in the temperature range. Only one glass transition temperatures $T_g$, onset crystallization temperature $T_c$ and the peaks of crystallization $T_p$. The thermal annealing applied to the sample of $\text{As}_{47.5}\text{Se}_{47.5}\text{Ag}_{5}$ thin films at five various annealed temperatures 463, 532, 604, 613, and 623 K, respectively, with a heating rate of 20 K/min at a fixed time (30 min) under nitrogen gases in the range of glass transition temperature and maximum crystallization temperature of composition under studied (see Fig. 1). The thickness of the annealed samples were calculated in terms of envelop method, it was 1383 nm (for more details see Ref. [3]). XRD was used to monitoring the transformation from amorphous to gradually crystalline thin films as shown in Fig. 2. One can see the films annealed at 532 K are typically still in amorphous state.

The increase of the annealing temperatures till the onset temperature (at 604 K) leads to that the film starts to convert from amorphous state to crystalline state. The sharpness of the intensity of the peaks increase with increase of the annealing temperature. This means that the thermal annealing leads to the rearrangement atoms and eliminates the crystal defects in the film. The X-ray diffraction patterns of the annealed films show a presence of AsSe, $\text{AgAsSe}_2$, and $\text{Ag}_2\text{Se}$ phases. The main crystalline phase is AsSe with (M: monoclinic) crystal structure with a unit cell defined by $a = 0.669$ nm, $b = 0.1386$ nm and $c = 1$ nm according to the ICDS [card no. (00-037-1122)] [18]. Another two crystalline phases of $\text{AgAsSe}_2$ (T: tetragonal) and $\text{Ag}_2\text{Se}$ (O: orthorhombic) appear with increase of the annealing temperature according to cards numbers [card no. (00-033-1165)], [card no. (01-071-2410)], respectively, [19, 20]. Table I shows the comparative interplanar spaces for both typically ($d_{exp}$) and standard ($d_{stand}$) cards for all phases that appear with increase of the annealing temperatures.
The X-ray structure data, phases observed, crystallite size $D$, dislocation density $\delta$, and strain $\varepsilon$ of different annealing temperatures for $\text{As}_{47.5}\text{Se}_{47.5}\text{Ag}_5$ thin films. (M: monoclinic, T: tetragonal, O: orthorhombic)

<table>
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<tr>
<th>Annealing temp. [K]</th>
<th>$d_{\text{exp.}}$ [Å]</th>
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<th>$hkl$ plane</th>
<th>Crystallite size $D$ [nm]</th>
<th>Strain, $\varepsilon \times 10^{-4}$</th>
<th>Dislocation density, $\delta \times 10^{14}$ [m$^{-2}$]</th>
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</table>

In terms of XRD pattern, the crystallite size $D$, dislocation density $\delta$, and the micro-strain $\varepsilon$ can be calculated as a function of annealing temperature, which plays an important role in several properties such as thermal stability and mechanical properties. The average crystallite size $D$ of all crystalline phases was calculated according to Scherrer’s equation [21]:

$$ D = \frac{K\lambda}{\beta \cos \theta}, $$

where $K$ is a shape factor known as the Scherrer constant normally equal to 0.94 and $\beta$ is the full width at half maximum (FWHM) of the peak. The dislocation density “$\delta$” (i.e. the dislocation lines per unit area) of the crystal can be calculated once the crystallite size “$d$” is estimated using the formula [22]:

$$ \delta = \frac{1}{D^2}. $$

On the other hand, the origin of the strain is also related to the lattice mismatch and may be calculated from the following relation [23]:

$$ \varepsilon = \left( \frac{\lambda}{D \cos \theta} - \beta \right) \frac{1}{\tan \theta}. $$

The calculated values of $D$, $\delta$, and $\varepsilon$ are listed in Table I. The values of the crystallite size are increased whereas the dislocation density and strain are decreased with increase of the annealing temperatures. This may be due to attributed to the decreasing in lattice defects among the grain boundaries [24, 25]. The dependence of the average crystallite size $D$, dislocation density $\delta$, and lattice strain $\varepsilon$, of the main AsSe phase formed as a function of annealing temperatures are shown in Fig. 3.

3.2. Absorption coefficient and optical band gap analysis

Figure 4 shows the variation of absolute spectral values of reflectance $R$ and transmittance $T$ versus wavelength $\lambda$ for both deposited and annealed of $\text{As}_{47.5}\text{Se}_{47.5}\text{Ag}_5$ thin film. One can notice that the transmittance increases with increase of the annealing temperature and the absorption edge shifted towards higher wavelength due to changes in the structural properties of the films owing to the increase of annealing temperature. The absorption
Fig. 3. The thermal processes dependence of the crystallite size $D$, dislocation density $\delta$ and strain $\varepsilon$ of AsSe phase formed in $\text{As}_{47.5}\text{Se}_{47.5}\text{Ag}_5$ thin films.

Fig. 4. (a) The optical transmittance $T_\lambda$ and reflectance $R_\lambda$ spectrum of as prepared and different annealing temperatures for $\text{As}_{47.5}\text{Se}_{47.5}\text{Ag}_5$ thin films. (b) The red shift of transmission spectra in strong absorption region of as prepared and different annealing temperatures for $\text{As}_{47.5}\text{Se}_{47.5}\text{Ag}_5$ thin films.

The absorption coefficient $\alpha$ can be calculated in strong absorption region using both transmission $T$ and reflection $R$ spectra [20]:

$$\alpha = \frac{1}{d} \ln \left( \frac{(1 - R)^2 + \sqrt{(1 - R)^4 + 4(TR)^2}}{2T} \right),$$

(4)

where $d$ is the thickness of the films that can be determined by Swanepoel’s method (mentioned below). Figure 5 shows the variation values of the absorption coefficient $\alpha$ versus photon energy $h\nu$ as a function of annealing temperature for $\text{As}_{47.5}\text{Se}_{47.5}\text{Ag}_5$ thin film. The absorption edge shifts towards the lower photon energies. It is clear that the absorption edge ($\alpha \geq 10^4$) shifts towards the lower photon energy with increase of the annealing temperature that is related to the decrease of the optical band gap.

According to the Tauc relation at the end of absorption edge region ($\alpha \geq 10^4$ cm$^{-1}$) [27] the optical energy band gap $E_g$ can be calculated using the values of the absorption coefficient $\alpha$:

$$\alpha(h\nu) = \frac{B(h\nu - E_g)^r}{h\nu},$$

(5)

where $B$ is a constant parameter dependent on the transition probability and $r = 1/2$ for direct transition band gap and $r = 2$ for non-direct transition band gap. For all different annealing temperatures (463, 532, and 604 K) of $\text{As}_{47.5}\text{Se}_{47.5}\text{Ag}_5$ thin films the indirect transitions are valid and the direct transitions are valid.

In this study the direct transition is valid for annealed $\text{As}_{47.5}\text{Se}_{47.5}\text{Ag}_5$ thin films after the inset of crystallization temperatures at 613 and 623 K. For all different annealing temperatures 463, 532 and 604 K of $\text{As}_{47.5}\text{Se}_{47.5}\text{Ag}_5$ thin films the indirect transitions and the direct transitions are valid. Figure 6 shows the $(\alpha h\nu)^{1/2}$ vs. $h\nu$ for as-deposited and annealing temperatures 463, 532 and 604 K while the
Structural and Optical Constants of Annealed As\textsubscript{47.5}Se\textsubscript{47.5}Ag\textsubscript{5} Film Using DSC Transformation Curve

Fig. 6. The plots of indirect transitions and direct transitions with the photon energy $h\nu$ of as prepared and annealed different temperatures for As\textsubscript{47.5}Se\textsubscript{47.5}Ag\textsubscript{5} thin films.

$(\alpha h\nu)^2$ vs. $h\nu$ for annealing temperatures 613 and 623 K. The optical energy band gap $E_g$ of the films was evaluated from the intercept of linear portion of each curve for different annealing temperature with the $h\nu$ in the abscissa, i.e. at $(\alpha h\nu)^{1/2} = 0$, $(\alpha h\nu)^2 = 0$, respectively, see in Fig. 6. The annealing process confirmed the crystallinity of the films. Furthermore, the increase of the annealing temperature may increase the crystallite size. Therefore, the decrease in the energy band gap may be attributed to quantum confinement phenomena.

Moreover, the absorption coefficient at less than about $\alpha \approx 10^4$ cm$^{-1}$ near the absorption edge depends exponentially on $h\nu$ as [28]:

$$\alpha(h\nu) = \alpha_0 \exp \frac{h\nu}{E_e},$$

where $\alpha_0$ is a constant, $E_e$ is the Urbach energy and is determined from plotting $\ln \alpha$ vs. $h\nu$ as shown in Fig. 7. The deduced values of the band gap, $E_g$ and $E_e$ (obtained from the slope of the straight lines of Fig. 7), are listed in Table II. It is evident from the results that the values of $E_g$ decrease with increase of annealed temperature while the Urbach energy $E_e$ increases with increase of annealed temperature. This may be as a result to the increase of the lattice parameter and hence the unit cell size, also the amorphous-crystalline transformations after annealing are responsible for decrease of the film optical gap [5, 25, 29].

3.3. Refractive index and dispersion parameters

The refractive index $n$ of the annealing films under study can be calculated according to envelope method using transmission spectrum proposed by Swanepoel [30, 31]. Figure 8 illustrates the transmittance spectrum for annealing temperature 463 K. As example using this method the same procedure was applied to the other different annealing temperatures. The refractive index $n$ can be deduced at any wavelength using the formula

$$n = \sqrt{N + (N^2 - s^2)^{1/2}},$$

TABLE II

<table>
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<tr>
<th>Annealing temperature [K]</th>
<th>Cauchy coefficient $E_g$ [eV]</th>
<th>$E_e$ [eV]</th>
<th>$E_d$ [eV]</th>
<th>$E_o$ [eV]</th>
<th>$n_o$</th>
<th>$\varepsilon_o$</th>
<th>$\varepsilon_l$</th>
<th>$s_o \times 10^{13}$ [m$^2$]</th>
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where
\[
N = 2s \frac{T_M - T_m}{T_M T_m} + \frac{s^2 + 1}{2},
\]
\[
s = \frac{1}{T_s} + \left( \frac{1}{T_s^2} \right)^{1/2}.
\] (8)

\(T_M\) and \(T_m\) are the transmittance maximum and minimum, respectively, at a certain wavelength. The procedure adopted to deduce the refractive index \(n\) of as-prepared thin films, see our previous published work [3].

The dependence of refractive index \(n\) with wavelength for all annealing temperatures thin films under studied are evident in Fig. 9. In the strong absorption spectral region, the values of the refractive index \(n\) can be fitted using the two-term Cauchy dispersion relationship, \(n(\lambda) = a + b/\lambda^2\), which can be used for extrapolating the complete overall wavelengths [32] (see solid lines in Fig. 9). Figure 9 shows that with increase of the annealing temperature the refractive index \(n\) decreases. This behavior may be attributed to the reduction of the number of unsaturated defects, which causes the reduction in the density of localized states in the band structure consequently decreasing the refractive index [33]. The values of Cauchy coefficient \(A\) and \(B\) are clear in Table II. Furthermore, the values of extinction coefficient \(k\) can be calculated from the absorption coefficient \(\alpha\) and wavelength \(\lambda\) values using the formula \(k = \alpha \lambda / 4\pi\). Figure 10 shows the extinction coefficient versus the wavelength for \(\text{As}_{47.5}\text{Se}_{47.5}\text{Ag}_5\) thin film at different temperature of annealing. It is clearly seen that the extinction coefficient increases with increase of the annealing temperature.

Now, the values of dispersion refractive index for \(\text{As}_{47.5}\text{Se}_{47.5}\text{Ag}_5\) thin films at different annealing temperature can be analyzed according to the single-oscillator model suggested by the Wemple–DiDomenico (WDD) by the relation [16]:
\[
n^2 = 1 + \left( \frac{E_o E_d}{E_o^2 - (h\nu)^2} \right),
\] (9)
where \(E_o\) is the single-oscillator energy and \(E_d\) is the dispersion energy. The plot of \((n^2 - 1)^{-1}\) vs. \((h\nu)^2\) is shown in Fig. 11. The values of \(E_o\) and \(E_d\) are determined from the intercept \(E_o/E_d\) and the slope \((E_o E_d)^{-1}\) of the straight lines. Further, it is obviously found that \(E_o\) de-
Structural and Optical Constants of Annealed As\textsubscript{47.5}Se\textsubscript{47.5}Ag\textsubscript{5} Film Using DSC Transformation Curve

Fig. 11. Plots of $1/(n^2-1)$ versus $hv$ for As\textsubscript{47.5}Se\textsubscript{47.5}Ag\textsubscript{5} thin films at various annealed temperatures.

Fig. 12. Plots of $n^2$ versus $\lambda^2$ for As\textsubscript{47.5}Se\textsubscript{47.5}Ag\textsubscript{5} thin films at various annealed temperatures.

Fig. 13. Plots of $1/(n^2-1)$ versus $\lambda^{-2}$ for As\textsubscript{47.5}Se\textsubscript{47.5}Ag\textsubscript{5} thin films at various annealed temperatures.

CREASES, while $E_d$ increases with increase of the thermal annealed temperature as shown in Table II. The decrease of $E_o$ values reveals that the strength of the inter-band optical transitions decreases with increase of the thermal process. But the increase of the $E_d$ values with the annealed temperatures maybe attributed to the increase of the rate of diffusion of atoms in the films which gives more number of atoms at interstitial sites, this lead to impurity type scattering centers [34].

In order that deduce the high frequency dielectric constant ($\varepsilon_l$) we have further analyzed the data of refractive index dependence photon’s energy $hv$ through two procedures, the first is proceeding the relation between the lattice high frequency dielectric constant ($\varepsilon_l$) and the refractive index, $n$ that is given by the following relation [16]:

$$n^2 = \varepsilon_l - \frac{e^2 N \lambda^2}{4\pi\varepsilon_0 m^*},$$  \hspace{1cm} (10)

where $e$ is electron charge, $N$ is the number of free carriers to the effective mass $m^*$. Figure 12 shows the plots of $n^2$ vs. $\lambda^2$ for the different annealing temperatures. The values of $\varepsilon_l$ were determined from the intercept with the ordinate $\lambda^2 = 0$ and given in Table II.

Additionally, the static refractive index $n_o$ for all annealing temperatures was determined using the subsequent relation

$$n_o = (1 + E_d/E_o)^{1/2}. \hspace{1cm} (11)$$

Thus the values of zero-frequency dielectric constant $\varepsilon_o = n_o^2$ were deduced. The values of the $n_o$ and $\varepsilon_o$ for all the annealing temperatures for all films are listed in Table II. The values of $n_o$ and $\varepsilon_o$ increase with the increase of the thermal process and $\varepsilon_o < \varepsilon_l$. This behavior may be owing to the contribution of charge in the polarization process that occurs inside the material when the light is incident on it [25].

The second proceeding to deduce the inter-band oscillator wavelength ($\lambda_o$) and the oscillator strength ($s_o$) for As\textsubscript{47.5}Se\textsubscript{47.5}Ag\textsubscript{5} thin films at different annealing temperatures by using the single Sellmeier oscillator [35]:

$$\frac{n^2 - 1}{n^2 - 1} = 1 - \left(\frac{\lambda_o}{\lambda}\right)^2. \hspace{1cm} (12)$$

The values of $\lambda_o$ and $s_o$ for all annealing temperatures films were calculated from the slope and intercept of the plots of $(n^2-1)^{-1}$ vs. $\lambda^{-2}$ (see in Fig. 13) and were given in Table II. The values of parameters $\lambda_o$ and $s_o$ change with change of the annealing temperatures. These changes show that the film is suitable to change of refractive index and oscillator parameters by changing annealing temperature [16, 36].
4. Conclusions

X-ray diffraction has been used to examine the structures of the as-deposited and annealed As$_{47.5}$Se$_{47.5}$Ag$_5$ thin films. Swanepoel’s method has been introduced to find the film thickness, refractive index, and hence other optical constants. The results of XRD demonstrate that the crystallinity of the main phase AsSe is improved by increase of the annealing temperature in the range of crystallization area of DSC curve. Furthermore, the dislocation density and lattice strain decrease with increase of annealing temperatures. The decrease in the energy gap of As$_{5}$Se$_{5}$Ag$_{5}$ thin films at different annealing temperature can be determined in the strong absorption region and satisfied indirect transition for amorphous thin film and direct transition for annealed crystalline thin film. The optical band gap decreases with increase of the annealing temperature. The decrease in the optical band gap $E_g$ may be attributed to quantum confinement phenomena. Also, the refractive index decreases with increase of the annealing temperature. This behavior may be attributed to the reduction of the number of unsaturated defects, which causes the reduction in the density of localized states in the band structure. Finally, the dispersion parameters such as $E_E$, $E_o$, $\varepsilon_o$, $\varepsilon_l$, $s_o$ and $\lambda_o$ are sensitive to thermal processes.

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