

Comparative structural and optical properties of $\text{Ge}_2\text{Sb}_2\text{Te}_5$, $\text{In}_{0.3}\text{Ge}_2\text{Sb}_2\text{Te}_5$ and $\text{Se}_2\text{Sb}_2\text{Te}_6$ thin films

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Structural and optical properties of thermally evaporated $\text{Ge}_2\text{Sb}_2\text{Te}_5$, $\text{In}_{0.3}\text{Ge}_2\text{Sb}_2\text{Te}_5$ and $\text{Se}_2\text{Sb}_2\text{Te}_6$ thin films are reported. The structural analysis is investigated using X-Ray diffraction measurements from which the lattice constants are calculated and found to be greater for $\text{Se}_2\text{Sb}_2\text{Te}_6$ films than for $\text{Ge}_2\text{Sb}_2\text{Te}_5$. The refractive indices are deduced from optical transmission measurements whereas the optical band gap (E_g) is obtained from optical absorption measurements. It is found that $\text{Se}_2\text{Sb}_2\text{Te}_6$ film has higher optical band gap and lower refractive index than $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film. This could be attributed to the presence of selenium that has a wider energy gap than Ge. The addition of indium to $\text{Ge}_2\text{Sb}_2\text{Te}_5$ alloy leads to a slight increase in the refractive index and the optical gap, but no significant change on the lattice constant is observed.

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1. Introduction

The rapid growth of the multimedia technology has demanded fast and small rewritable nonvolatile memory devices as essential components. One of the most promising media for re-writable applications is phase-change materials. The idea to use an amorphous-to-crystalline phase transition for information storage established in the 1960s when S.R. Ovshinsky suggested a memory switch based upon changes in the properties of amorphous and crystalline phases of multicomponent chalcogenides¹. In 1990s this technology was commercialized when $\text{Ge}_2\text{Sb}_2\text{Te}_5$ was used as the recording medium in phase-change memory devices². Chalcogenides based phase-change materials have been extensively used in optical rewritable data storage media because of the discrete changes in their optical properties that occur due to the phase-change from the amorphous to the crystalline phase [3-7]. The difference in optical properties is essential to obtain a high contrast between amorphous and crystalline regions which enables a straight forward reading of the information.

Chalcogenide amorphous semiconductors, utilizes the resistivity difference between crystalline and amorphous phases. It is noted that a typical resistivity ratio between amorphous and crystalline phase is more than 1000 [8-10]. This huge difference in the resistivity establishes the phase-change memory as a good candidate for the next generation nonvolatile memory [11, 12]. The electrical switching between amorphous and crystal phases had been studied on Se-Sb-Te films, where its melting point is lower than that of the Ge-Sb-Te system [13]. Some properties of Se-Sb-Te crystalline structure were reported [7, 14], but there has been no report to date, as far as the authors can discern, about the optical properties of Se-Sb-Te films. Therefore, it is desirable to have a thorough understanding

of its structural and optical properties. In this paper, the transmission spectra of amorphous and crystalline phases of $\text{Se}_2\text{Sb}_2\text{Te}_6$ films are presented. The optical energy gap and the refractive index are calculated. Since the change in the optical and electrical properties is accompanied by a change in structural properties [15], x-ray diffraction measurements of crystalline $\text{Se}_2\text{Sb}_2\text{Te}_6$ film allow the determination of the lattice constant. The optical and structural measurements were conducted on Ge-Sb-Te films for comparison.

2. Experimental

Bulk alloys of $\text{Ge}_2\text{Sb}_2\text{Te}_5$, $\text{In}_{0.3}\text{Ge}_2\text{Sb}_2\text{Te}_5$, and $\text{Se}_2\text{Sb}_2\text{Te}_6$, are prepared by melt quenching technique. Materials (99.995% pure) are weighed according to their atomic percentage and sealed in quartz ampoules in a vacuum $\sim 10^{-3}$ mbar. The sealed ampoules are heated at 1050 °C for 24 hours. A cylindrical rotating furnace is used to mix the materials inside the ampoules to ensure homogeneity of the materials. Thereafter, the quenching is done in ice-water bath. Thin films are prepared by thermal evaporation at a base pressure of 10^{-5} mbar. The thicknesses of the films were 1.5 μm for $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and $\text{In}_{0.3}\text{Ge}_2\text{Sb}_2\text{Te}_5$ and 1.6 μm for $\text{Se}_2\text{Sb}_2\text{Te}_6$. The compositions of the evaporated films are identified by Energy Dispersive X-Ray (EDX). The samples were annealed at 200°C for 30 minutes to study the structural and optical properties in the crystalline phase. The structure of the films before and after annealing was investigated using X-Ray diffraction (XRD) spectroscopy (Philips diffractometer with CuK_α source). The optical measurements were performed using UV/VIS/NIR spectrophotometer (JASCO 670) in the range of 200 to 3200 nm (0.39 to 6.2 eV) photon energy.

3. Results and discussion

The X-Ray diffraction spectra of amorphous and crystalline phases of $\text{Ge}_2\text{Sb}_2\text{Te}_5$, $\text{In}_{0.3}\text{Ge}_2\text{Sb}_2\text{Te}_5$ and $\text{Se}_2\text{Sb}_2\text{Te}_6$ films are shown in Figs. 1(a), (b), and (c), respectively. There are no peaks shown in the amorphous phase while several peaks are observed in the crystalline phase.

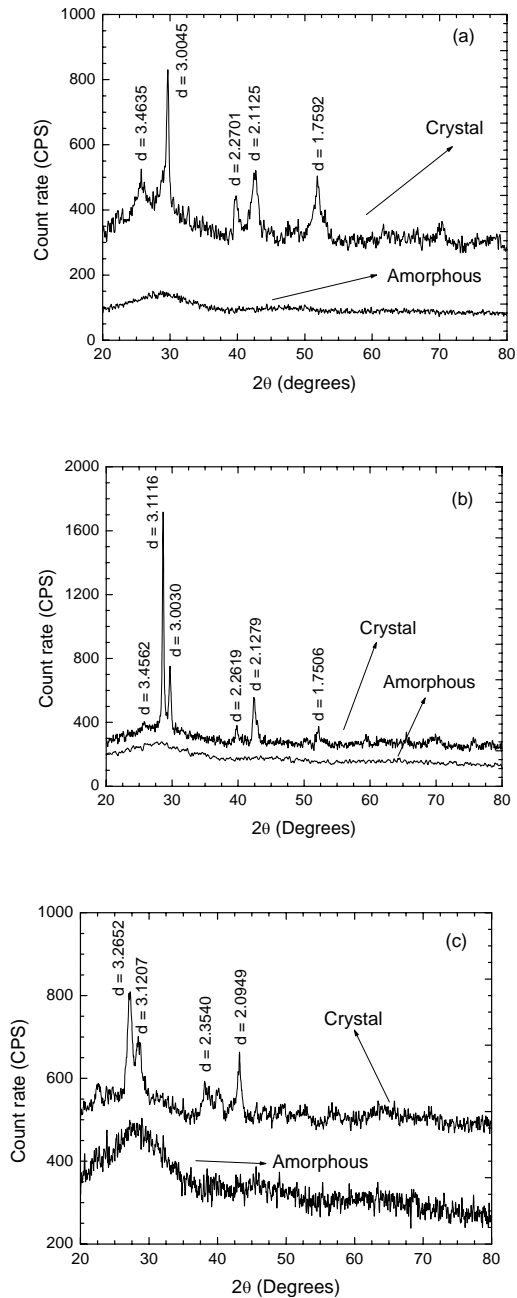


Fig. 1. X-Ray diffractograms of (a) $\text{Ge}_2\text{Sb}_2\text{Te}_5$, (b) $\text{In}_{0.3}\text{Ge}_2\text{Sb}_2\text{Te}_5$ and (c) $\text{Se}_2\text{Sb}_2\text{Te}_6$ films. The figure shows clearly the amorphous phase of the as-deposited films and the crystalline phase after annealing the films at 200°C .

The lattice constant (a) has been calculated from the inter-planner distances (d) shown in the figure. The values of the lattice constants are listed in Table 1. The values of Ge based films are in good agreement with those reported in literature [8, 16, 17]. Moreover, the lattice constant in Se-based film is greater than in Ge-based films. This could be attributed to the difference in the structure of the tow materials. Raman studies of amorphous Ge-Sb-Te alloys support the random covalent network model [18], in which Te, Sb and Ge have two-, three- and four-fold coordination, respectively. Hence, the crystalline structure and its' parameters are correlated to Te- chains segments cross-linked by a tetrahedral structure of Ge and Sb. On the other hand, the structure in Se-Sb-Te film is more dominated by chain segments of the two-fold coordinated atoms (Se and Te) that can be cross-linked by Sb only.

Table 1. The lattice constant, the refractive index, and the optical gap for amorphous and crystalline phases of the different films in the study.

Sample	Thickness (μm)	Lattice Constant (\AA)	Refractive Index (n)		Energy Gap (eV)	
			Amorphous	Crystalline	Amorphous	Crystalline
$\text{Ge}_2\text{Sb}_2\text{Te}_5$	1.5	6.009	4.04		0.71	0.5
$\text{In}_{0.3}\text{Ge}_2\text{Sb}_2\text{Te}_5$	1.5	6.01	4.13		0.72	0.61
$\text{Se}_2\text{Sb}_2\text{Te}_6$	1.6	6.658	3.28	4.02	0.88	0.6

Transmission spectra of the amorphous and crystalline states for $\text{Ge}_2\text{Sb}_2\text{Te}_5$, $\text{In}_{0.3}\text{Ge}_2\text{Sb}_2\text{Te}_5$ and $\text{Se}_2\text{Sb}_2\text{Te}_6$ films are shown in Figs. 2(a), (b), and (c), respectively. The figures show that at short wavelengths below $\lambda = 1000$ nm the transmission is approximately zero. The transmission increases as the wavelength increases and showing an interference pattern due to the reflected waves from the front and back surfaces of the film. The refractive index can be calculated from any two successive peaks of the interference pattern using the following equation [19]:

$$n = \frac{1}{\left[\frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right] x}, \quad (1)$$

where λ_1 and λ_2 are the wavelengths at two adjacent maxima and x is the film thickness. The refractive index of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ is $n = 4.04$ at wavelengths $\lambda_1 = 1540$ nm and $\lambda_2 = 2065$ nm and for thickness $x = 1.5$ μm . The refractive index of $\text{In}_{0.3}\text{Ge}_2\text{Sb}_2\text{Te}_5$ is $n = 4.13$ at wavelengths $\lambda_1 = 1500$ nm and $\lambda_2 = 1980$ nm and for thickness $x = 1.5$ μm . The refractive index of $\text{Se}_2\text{Sb}_2\text{Te}_6$ film is $n = 3.28$ at wavelengths $\lambda_1 = 1390$ nm and $\lambda_2 = 1890$ nm and for thickness $x = 1.6$ μm .

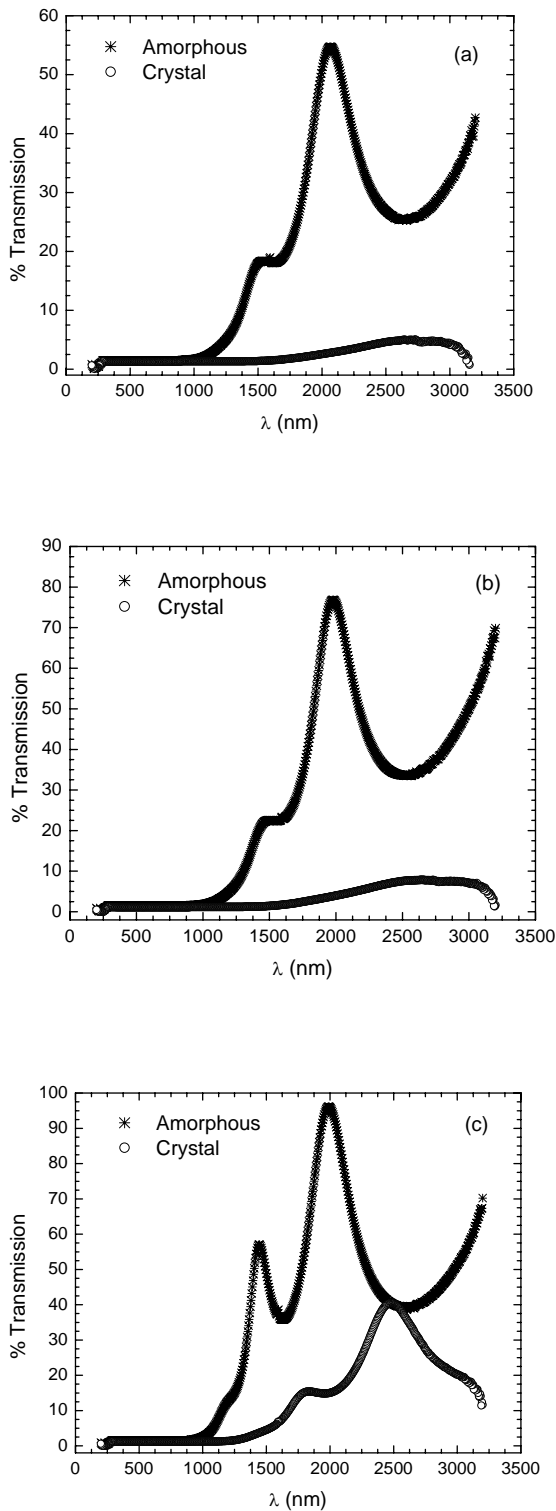


Fig. 2. Transmission spectra of (a) $\text{Ge}_2\text{Sb}_2\text{Te}_5$, (b) $\text{In}_{0.3}\text{Ge}_2\text{Sb}_2\text{Te}_5$ and (c) $\text{Se}_2\text{Sb}_2\text{Te}_6$ films.

In the crystalline phase, Ge-based films are very reflective, hence a very low transmission is observed as shown in figures 2(a) and (b). On the other hand, the reflectivity of Se-based film is less as depicted in figure 2(c) and the refractive index is calculated from the transmission spectrum. The refractive index of $\text{Se}_2\text{Sb}_2\text{Te}_6$ film is found to be 4.02 at wavelengths $\lambda_1 = 1800$ nm and $\lambda_2 = 2500$ nm. From the above results one can observe the following:

a) Indium doped $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film shows a slight increase in the refractive index. This could be attributed to the metallic properties of indium that makes wave propagation affected by its large conductivity.

b) The refractive index of Se-based film is less than Ge-based films. The presence of Se which has a wide band gap (2 eV) might be the reason that causes a smaller refractive index. This result is in good agreement with the experimental observations in other semiconductors [20].

c) The refractive index of $\text{Se}_2\text{Sb}_2\text{Te}_6$ film in crystalline phase is greater than amorphous phase as well known in literature [21].

The optical energy gap of semiconductors can be determined from transmission and reflection measurements. In addition to transmission (T) measurements, reflection (R) measurements have been performed using an "Integrating Sphere". The absorption coefficient has been deduced according to the following formula [19]:

$$T = (1 - R)^2 e^{-\alpha x} \quad (2)$$

The absorption coefficient of semiconductors is given by:

$$\alpha hv = \beta(hv - E_g)^r, \quad (3)$$

where α is the absorption coefficient, hv is the photon energy, β is constant and E_g is the energy gap. Tauc *et al.*, stated that $r = 2$ holds in amorphous semiconductors assuming parabolic bands; this behavior is found for many amorphous semiconductors [22].

The Tauc plot $(\alpha hv)^{1/2}$ versus the photon energy (hv) for $\text{Ge}_2\text{Sb}_2\text{Te}_5$, $\text{In}_{0.3}\text{Ge}_2\text{Sb}_2\text{Te}_5$ and $\text{Se}_2\text{Sb}_2\text{Te}_6$ films are shown in Figs. 3(a), (b), and (c), respectively. The linear extrapolation of the curve in Tauc plot yields the optical energy gap. The optical energy gaps (E_g) of the amorphous and crystalline phases of $\text{Ge}_2\text{Sb}_2\text{Te}_5$, $\text{In}_{0.3}\text{Ge}_2\text{Sb}_2\text{Te}_5$ and $\text{Se}_2\text{Sb}_2\text{Te}_6$ films are listed in table 1. It is shown that, there is no significant change in the optical energy gap due to the addition of indium in Ge-based films. Similar results have been reported in literature [21]. The substitution of Germanium by Selenium atoms increases the optical energy gap from 0.7 eV in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ to 0.88 eV in $\text{Se}_2\text{Sb}_2\text{Te}_6$ films owing to the selenium element has a higher energy gap than germanium. These results are similar to our previous results predicted by the relaxation frequency activation energy measurements [7]. Lower refractive index and higher energy gap in Se-based film than Ge-based films are in good agreement with the previously reported data on other semiconductors [20].

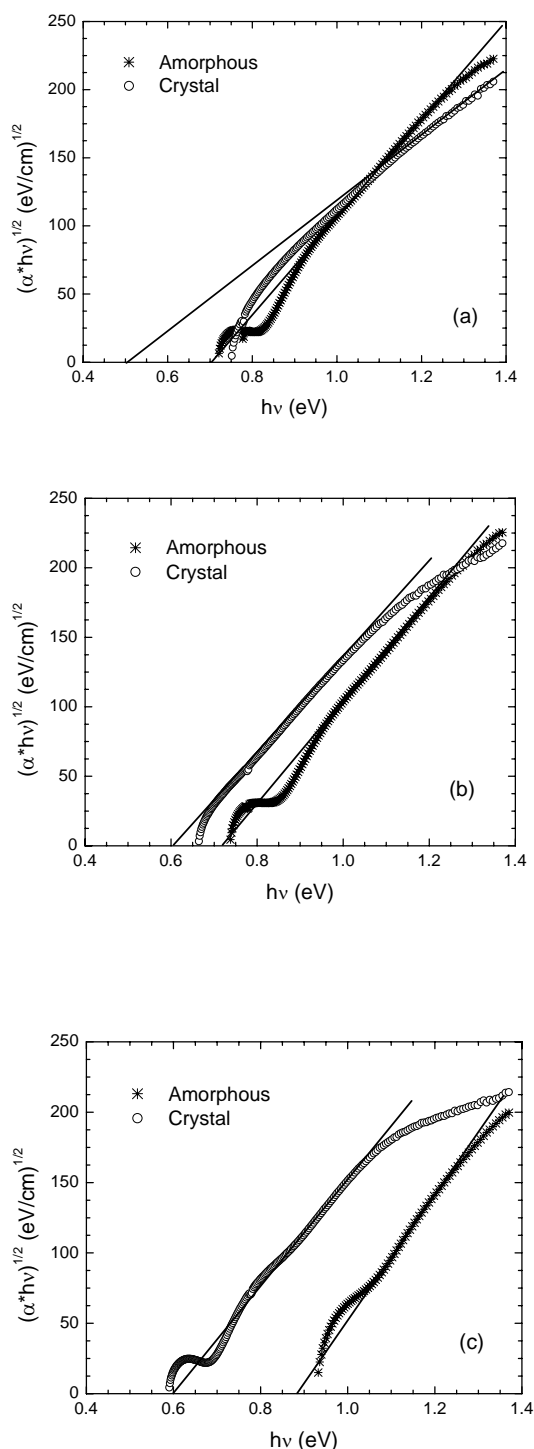


Fig. 3. Plots of $(\alpha * hv)^{1/2}$ against photon energy hv for (a) $Ge_2Sb_2Te_5$, (b) $In_{0.3}Ge_2Sb_2Te_5$ and (c) $Se_2Sb_2Te_6$ films. The intercept of solid lines with x-axis gives the estimated value of the optical energy gap.

In contrast, Ge-based and Se-based films are crystallized after annealing at higher temperatures than

their crystallization temperatures (T_c). The optical energy gaps of these films are listed in table 1. The measured optical energy gaps in the crystalline phase decrease as expected and reported in literature [23].

5. Conclusion

Structural and optical properties of $Ge_2Sb_2Te_5$, $In_{0.3}Ge_2Sb_2Te_5$ and $Se_2Sb_2Te_6$ thin films have been reported. The structural analysis is investigated using X-Ray diffraction measurements. The lattice constants are found to be $a = 6.009 \text{ \AA}$, $a = 6.01 \text{ \AA}$ and $a = 6.658 \text{ \AA}$ for $Ge_2Sb_2Te_5$, $In_{0.3}Ge_2Sb_2Te_5$ and $Se_2Sb_2Te_6$ films, respectively. The values of lattice constants of Ge-based films are in good agreement with the values reported in literature. The lattice constant in Se-based film is greater than Ge-based films due to structural differences of these materials.

The refractive indices of these films are obtained from the optical transmission measurements for amorphous and crystalline phases as shown in table 1. The refractive index of $In_{0.3}Ge_2Sb_2Te_5$ film is slightly greater than the refractive index of $Ge_2Sb_2Te_5$ film. Furthermore, the refractive index of Se-based film is less than Ge-based films.

The optical energy gaps $E_g = 0.71 \text{ eV}$, 0.72 eV and 0.88 eV for $Ge_2Sb_2Te_5$, $In_{0.3}Ge_2Sb_2Te_5$ and $Se_2Sb_2Te_6$ films in amorphous phases, respectively. It is noted that, indium doped Ge-based film slightly increases the optical energy gap while the Se-based film has higher energy gap.

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