Chalcogenide Letters Vol. 15, No. 5, May 2018, p. 255 - 260

INVESTIGATIONS OF HEAT TREATMENT ON STRUCTURAL AND OPTICAL PROPERTIES OF $Ge_8Se_{60}Te_{30}In_2$ THIN FILM FOR OPTICAL DATA STORAGE

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Chalcogenide glasses of $Ge_8Se_{60}Te_{30}In_2$ were synthesized by melt quench process. Thin film of prepared glassy alloy was made by thermal evaporation method. To verify the glassy nature of the prepared sample differential scanning calorimetric (DSC) measurement whereas to investigate the phase transformation X-ray diffraction (XRD) measurement has been done. Annealing induced result on optical constants of prepared film has been explored using UV-Vis Spectrophotometer in the wavelength span 300 to 1100 nm. It is noticed that optical bandgap (E_g) and steepness parameter (σ) reduces while the absorption coefficient (α), extinction coefficient (k) and Urbach energy(E_e) increases with the increase of annealing temperature. It is observed that prepared sample obey the allowed direct transition. The reduction in optical bandgap with annealing temperature has been explained using Mott and Davis model. Due to annealing dependence of the optical constants, the investigated material could be utilized for optical data storage.

(Received March 6, 2018; Accepted May 8, 2018)

Keywords: Amorphous semiconductor, Thin films, Optical properties, Absorption coefficient, Optical band gap

1. Introduction

There is no doubt that silicon technology has received a great attention in modern technology but the development made by amorphous semiconductors (especially chalcogenide glasses) is, nevertheless, surprising and fascinating [1-2]. In the last few decades chalcogenide glasses put forward an interesting and exciting new platform for evolving all optical signal processing for the photonic devices [3].

Chalcogenide glasses have received a great deal of attention due to their potential applications in fiber optics, solar cell, memory device, IR photo detectors and bio-sensors [3–7]

In the present paper $Ge_8Se_{60}Te_{30}In_2$ composition is chosen because of various reasons. Pure selenium has broad commercial significance and device applications viz. photocells, memory switching and rectifiers [1-3]. However, low sensitivity and short lifetime are the drawbacks of pure selenium. To minimize these problems, many researchers have used various modifiers (Ga, Ge and Bi) for combining Se to few extents [8,9].

Amorphous to crystalline phase transformation based optical data storage uses the enormous changes in optical absorption and optical reflectivity in semiconductor thin films by heat treatment. Because of technological importance, effect of several radiations like thermal annealing, photo induced, laser irradiation, ultraviolet irradiation etc. on structural, optical and electrical properties of chalcogenide glasses have been subjected to a lot of study.

The present paper investigates the annealing induced effect on optical characteristics of prepared $Ge_8Se_{60}Te_{30}In_2$ chalcogenide thin films. In the prepared glassy alloy, selenium is taken in large amount because of its wide applications and commercial importance in electronic and optoelectronic field. Also, Se is transparent in the infrared span, good mechanical, chemical and thermal characteristics. Here Ge is used as an additive material with Se because of its contribution in long-term stability at room temperature [9]. Tellurium(Te) is added as third element to form

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chemical and topological disorder in Ge-Se alloys [9,10]. Indium (In) as a fourth element has obtained an exceptional and substantial interest because of its possible applications in many digital electronic devices [11,12].

2. Experimental details

Chalcogenide glasses of $Ge_8Se_{60}Te_{30}In_2$ were synthesized by melt quench process. High purity (99.999%) compositions were weighed in accordance with their atomic proportion with the help of an electronic balance (LIBOR, AGE-120) and poured in quartz ampoules. Least count of electronic balance was 10^{-4} gm. To prevent contamination by oxygen at high temperature, ampoule was evacuated by vacuum upto 10^{-5} torr and then sealed by sharp flame of LPG with oxygen. Sealed ampoule was kept in the rocking furnace and heated upto 1073K for 12h. Constant rocking was done to ensure homogeneity of alloy. Sudden quenching was done in ice-cold water to form the glassy alloy. Thin films of glassy composite of Ge-Se-Te-In were developed by thermal evaporation method. Film thickness was 400nm measured by quartz crystal thickness monitor. Indus-2 (RRCAT-Indore), BL-12 synchrotron radiation (λ=1.5406Å, $2\theta=9^o$-35^o) was used for X-Ray diffraction pattern.

To ascertain the crystallization temperature (T_c) and glass transition temperature (T_g) differential scanning calorimetric (DSC, MDSC-2910, TA instruments) measurement was taken on powder sample of Ge-Se-Te-In under pure N_2 atmosphere. Prepared thin films of $Ge_8Se_{60}Te_{30}In_2$ were annealed at three different temperatures (373K, 393K and 413K) for 2h in the presence of vacuum of 10^{-4} mbar. The three annealing temperature was taken in between the T_c and T_g recorded by DSC measurement. Normal incidence spectra of the prepared films were taken by double beam UV-Vis spectrophotometer (ECIL-Hyderabad, India, Model No: 5704ss) in the wavelength range of 300- 1100nm

3. Results

3.1. Structural properties

Typical DSC trace of $Ge_8Se_{60}Te_{30}In_2$ chalcogenide glass at 10K/min heating rate is displayed in Fig. 1. Two peaks are noticed in the DSC curve of the prepared sample. The first peak is an endothermic peak known as glass transition temperature at T_g = 88.48°C while the second is an exothermic peak corresponding to the peak temperature of crystallization at T_c = 176.91°C. The single glass transition peak indicates homogeneity of the prepared glass samples.

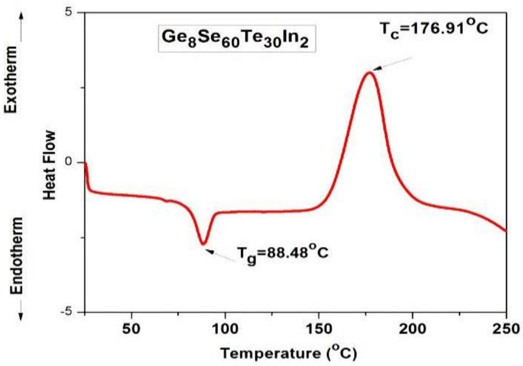

Fig 1. DSC thermogram for $Ge_{10}Se_{60}Te_{30}In_2$ glassy alloy

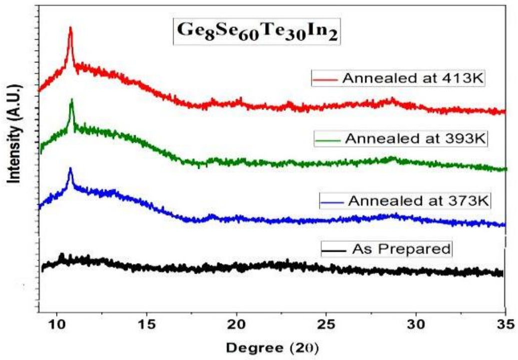

Fig 2. XRD pattern of as prepared and annealed $Ge_8Se_{60}Te_{30}In_2$ thin films

As shown in the Fig 2, the XRD of the as-prepared sample do not contain any sharp peak, which shows the typical amorphous nature of the prepared sample. It implies that during sample preparation there is no formation of nuclei. XRD pattern of the annealed films indicate the existence of crystalline peaks. This indicates that the heat treatment causes the amorphous-crystalline phase transformation.

3.2. Optical properties

One of the most fascinating optical properties of thin films is the process of absorption. The optical band gap of the semiconductor can be determined by the absorption process. Absorption of the material generates charge carriers which change the conductance [13]. In the absorption edge spectra of amorphous semiconductors, absorption process can be dividing in three well-defined regions. The first region is called weak absorption tail, which rises from defects and impurities. Second region is called exponential edge, which is associated to the structural randomness of the amorphous compound. Third is the high absorption region which is important to determine the optical energy gap width.

The absorption coefficient (α) is evaluated by the equation (1) [14-16].

$$\alpha = \frac{\mathrm{OD}}{\mathrm{t}} \tag{1}$$

Where, OD denotes optical density and t denotes layer thickness. Absorption coefficient (α) versus wavelength (λ) for as prepared and annealed films of $Ge_8Se_{60}Te_{30}In_2$ are depicted in Fig 3.

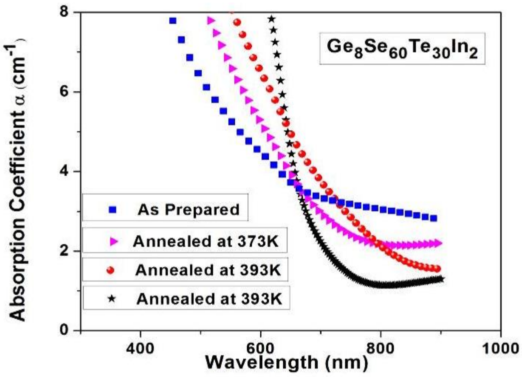

Fig 3. Absorption coefficient(α) versus wavelength (λ) in $Ge_8Se_{60}Te_{30}In_2$ thin film

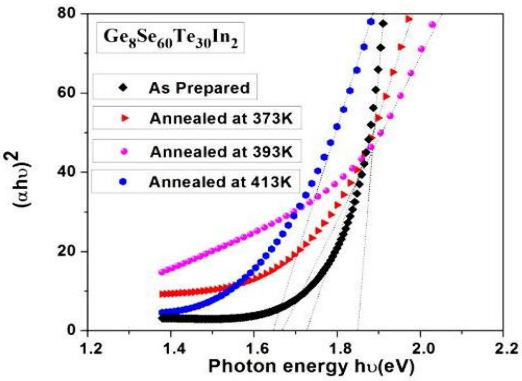

Fig. 4. $(\alpha h\nu)^2$ *versus photon energy (hν) in as prepared and annealed* $Ge_8Se_{60}Te_{30}In_2$ *thin film*

In most of the amorphous semiconductor, fundamental absorption follows the exponential law. Absorption coefficient obeys the well-known Tauc[17] relation above the exponential tails.

$$(\alpha h\nu)^{1/m} = A(h\nu - E_g) \quad (2)$$

where A is a constant which is associated with edge width parameter, optical band gap is E_g and m is an index which denotes type of electronic transition. m =1/2, 3/2, 2 and 3 correspond to allowed direct transition, forbidden direct transition, allowed indirect transition and forbidden indirect transition respectively [17]. In the present studied $Ge_8Se_{60}Te_{30}In_2$ thin films, equation (2) best fits the experimental results when m=1/2 shown in Fig 4. The calculated values of absorption coefficient and optical band gap at different heating treatment are mentioned in Table 1. The reduction in the energy gap (E_g) with heat treatment may be described by using Mott and Davis Model[18] according to which there is formation of surface dangling bonds throughout the crystallites in crystallization process.

The band tails width of localized states (E_e) near the band edges can be evaluated using Urbach's empirical relation [19]

$$\alpha = \alpha_0 \exp(h\nu/E_e) \quad (3)$$

Where α_0 is a constant, and E_e is the Urbach energy, hυ is the photon energy and α is the absorption coefficient. Variation of $\ln(\alpha)$ versus photon energy (hν) for as prepared and annealed $Ge_8Se_{60}Te_{30}In_2$ thin films

From the Urbach energy, the steepness parameter σ which characterizes the broadening of the absorption edge due to the electron-phonon interaction or excitation- phonon interaction can be calculated using the relation.

$$\sigma(T) = \sigma_o\left(\frac{2K_B T}{h\omega_p}\right)\tanh\frac{h\omega_p}{2K_B T} \quad (4)$$

σ_o is a parameter depend on the material. $h\omega_p$ corresponds to energy of photon associated with Urbach tail[20,21] and $K_B T/\sigma$ is called Urbach (E_e) energy. Therefore, we can get the relation

$$\sigma = (K_B T/E_e) \quad (5)$$

Where K_B is Boltzman constant and T is the absolute temperature.

Variations of steepness parameter σ with annealing temperatures is listed in Table 1.

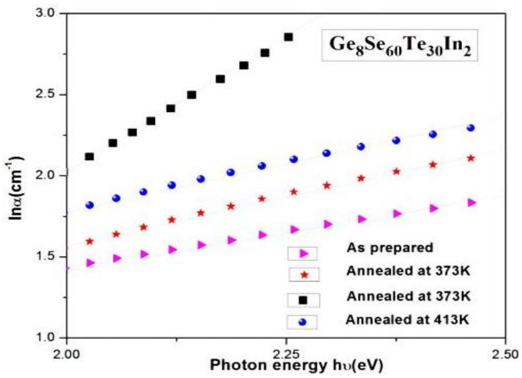

Fig. 5. Variation of $ln(\alpha)$ versus photon energy (hν) in as prepared and annealed $Ge_8Se_{60}Te_{30}In_2$ thin films

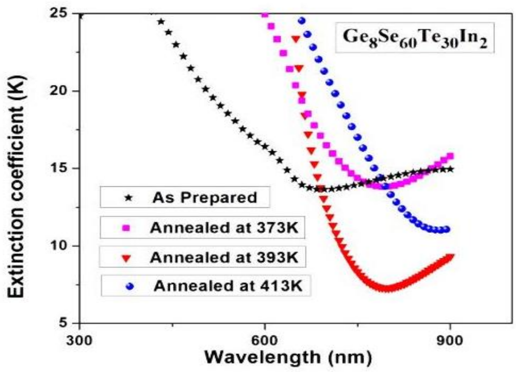

Fig. 6. Extinction coefficient (k) versus wavelength (λ.) in as prepared and annealed $Ge_8Se_{60}Te_{30}In_2$ thin film

Table1. Optical constants(α,k, E_g, E_e and σ) for as prepared and annealed $Ge_8Se_{60}Te_{30}In_2$ thin film

Sample $Ge_8Se_{60}Te_{30}In_2$	**Absorption coefficient α x 10^4 (cm^{-1})**	**Extinction coefficient (k)**	**Band gap E_g(eV)**	**Urbach energy E_e(eV)**	**Steepness parameter σ**
As prepared	4.14	24.01	1.87	0.68	5.54
Annealed at 373K	4.64	21.49	1.72	1.00	5.14
Annealed at 393K	5.80	19.26	1.65	1.08	5.02
Annealed at 413K	7.26	13.92	1.62	1.14	4.99

S. Hasegawa et al [22] proposed that thermal annealing crystallizes the ideal amorphous solids and dangling bonds are produced throughout the surface of crystallites during crystallization process. Further annealing breaks the crystallites into smaller crystals, thereby increasing the number of surface dangling bonds [22]. These dangling bonds are responsible for the creation of some types of defects in the highly polycrystalline solids. As the number of dangling bonds and defects increases with increase of annealing temperature, the concentration of localized states in the band structure also increases gradually. Hence, annealing of the films causes an increase in the energy width of the localized state thereby reducing the optical energy gap. Our results are in good agreement with recently reported results by other workers [9, 13].

The extinction coefficient is directly obtained by the relation

$$k = \frac{\alpha\lambda}{4\pi} \tag{6}$$

where, α denotes absorption coefficient and λ shows wavelength of photon. Fig. 6 show that extinction coefficient decreases with increase of annealing temperature. The obtained value of extinction coefficient at wavelength 660nm is listed in Table 1.

4. Conclusions

Thin film of a new quaternary $Ge_8Se_{60}Te_{30}In_2$ chalcogenide glasses were developed on glass substrate by thermal evaporation technique. The DSC and XRD studies show amorphous behavior of as prepared film and phase transformation in annealed films. It is noticed that the obtained value of α and k at particular wavelength increases with increasing the annealing temperatures.

The value of E_g and steepness parameter σ decreases with increase of annealing temperature. This reduction of optical bandgap with annealing temperature was described with the help of well-known Mott and Davis model for amorphous to crystalline phase transformations.

Acknowledgments

Authors are thankful to UGC- DAE CSR Lab Indore and Indus Beamline, RRCAT Indore, for providing financial assistance and experimental facility of DSC and XRD measurements.

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