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EFFECT OF LASER IRRADIATION ON THE OPTICAL PROPERTIES OF AMORPHOUS $Se_{96-x}Te_4Ga_x$ THIN FILMS

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Amorphous $Se_{96}Te_4$ and $Se_{94}Te_4Ga_2$ thin films were prepared onto glass substrates by using thermal evaporation method. The changes in the optical properties (optical band gap, absorption coefficient, and extinction coefficient) have been measured in the wavelength range 350-900 nm by a spectrophotometer. These thin films are irradiated by pulsed nitrogen laser up to ~7min. Optical band gap, extinction coefficient and absorption coefficient of these films have been studied before and after laser irradiation. It is found that optical band gap (Eg) is decrease in both cases after laser irradiation on thin amorphous film and increase by addition of Ga.

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Keywords: Amorphous semiconductors, Optical band gap, Chalcogenide glasses, Laser irradiation

1. Introduction

Recent advances and trends in the field of chalcogenide semiconductors reveal applications in xerography, switching and memory devices, and reversible phase change optical regarding [1-6]. The properties of chalcogenide glassy semiconductors are usually affected by the addition of third element. Experimental results reported by various workers have been shown that the addition of impurity atoms in binary Se-Te systems does change the optical properties of chalcogenide glassy semiconductors. Several workers [7-8] have reported the impurity effects in the various chalcogenide glasses. Exposure to light or other radiation that excites electron-hole pairs produces structural changes in nearly all chalcogenide glasses and amorphous films. This results in a change of atomic configuration, and a subsequent change in the physical and chemical properties such as structure, optical and electronic transport properties of the material [9-10]. The optical band gap, refractive index and extension coefficient are the most significant parameters in amorphous semiconducting thin films. The optical behavior of material is utilized to determine its optical constants. The objective of the present work is to investigate the effect of laser irradiation on the optical properties of various chalcogenide films such as $Se_{96}Te_4$ and $Se_{94}Te_4Ga_2$.

2. Experimental details

In the present research work, we choose melt quenching technique to prepare the $Se_{96-x}Te_4Ga_x$ (x = 0, 2) chalcogenide glass. The appropriate amounts of highly pure (99.999%) constituent element, in accordance with their atomic percentages were weighted using an electronic balance. The materials were then sealed in quartz ampoules (length ~ 10 cm and internal diameter ~0.8 cm) in a vacuum of $\sim 10^{-5}$ torr. The sealed ampoules were kept inside a programmable muffle furnace, where the temperature was raised to 900 ^{o}C at a rate of 5 ^{o}C min^{-1} for 10 h. The ampoules were frequently shaken by rotating a ceramic rod to which the ampoules

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was taked away of the furnace, to achieve better homogeneity. The molten sample was then rapidly quenched in ice cooled water. So obtained ingots of materials was grinded into its powder form by pestle and mortar.

Thin films of glassy alloy of $Se_{96}Te_4$ and $Se_{94}Te_4Ga_2$ of thickness 4000 Å were deposited on glass substrate in the shape of squares by using the vacuum evaporation technique at room temperature (300 K) and vacuum of $\sim 10^{-5}$ Torr, using a molybdenum boat. Films were kept inside the deposition chamber for 24 h to achieve metastable equilibrium. The thickness of the film was measured under a single-crystal thickness monitor. The amorphous thin films were induced by pulsed TEA N_2 laser (wavelength 337.1 nm, Power 100 kW, Pulse width 1 ns) for 7 min. For measuring optical absorption and % transmittance of thin films, a double beam, UV/VIS/NIR Spectrophotometer (Hitachi U 3400) was used. The optical absorption was measured as a function of wavelength (350-900 nm) of incident light.

3. Results and discussion

The measurement of the absorption coefficient α as a function of frequency ν of the incident beam provides a mean to determine the band gap E_g of a material. The absorption coefficient α has been calculated directly from the absorbance against wavelength curve using the relation [11-12]

$$\alpha = \frac{OD}{t}$$

Where OD is the optical density measured at a given thickness (t).

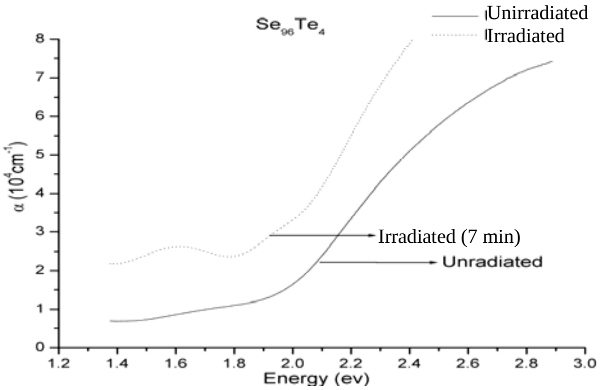

Fig. 1. Variation of α with photon energy (hν) for irradiated and un-irradiated $Se_{96}Te_4$ thin film.

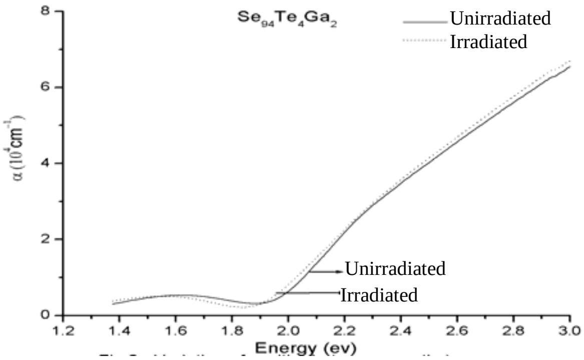

Fig. 2. Variation of α with photon energy (hν) for irradiated and un-irradiated $Se_{94}Te_4Ga_2$ thin film.

Figs. 1 and 2 shows the variation of absorption coefficient (α) as a function of incident photon energy ($h\nu$) for $Se_{94-x}Te_4Ga_x$ films before and after irradiation. It is found that the value of absorption coefficient is decreases with increase Ga. The absorption coefficient of these films are high ($\approx 10^4$ cm^{-1}) and are given in table 1.

Table 1. Optical parameters of a-$Se_{96-x}Te_4Ga_x$ system at 600 nm.

S.N.	Sample	Un-irradiated			Irradiated		
		α (10^4cm^{-1})	k	E_g (ev)	α (10^4cm^{-1})	k	E_g (ev)
1-	$Se_{96}Te_4$	2.0446	0.0977	1.59	3.7405	0.1787	1.47
2-	$Se_{94}Te_4Ga_2$	1.5672	0.0505	1.80	1.0499	0.0502	1.76

The optical band gaps of these systems $Se_{96}Te_4$ and $Se_{94}Te_4Ga_2$ were determined with the help of absorption spectra. The present system obeys the rule of indirect transition. As per well known relation of Tauc [13], the absorption coefficient for indirect band gap materials is given by

$$\alpha h\nu = A\,(h\nu - E_g)^2 \tag{2}$$

Where $h\nu$ is the photon energy, E_g is the band gap and A is constant.

Variation of $(\alpha h\nu)^{1/2}$ with photon energy ($h\nu$) for $Se_{96-x}Te_4Ga_x$ with unirradiated and irradiated films are shown in Fig. 3 and Fig. 4. The value of the indirect band gap has been detemined by taking the intercept on the x-axis. It is clear that optical band gap decreases after irradiation, and calculated values are given in Table 1. It is also clear from table that optical energy gap (E_g) increases with increase in Ga concentration in the $Se_{96-x}Te_4Ga_x$ system. The increase of band gap suggests [14] a decrease in the density of localized states. In chalcogenide materials the lone pair orbital forms the valence band, whereas the conduction band is formed by the antibonding orbital [10].

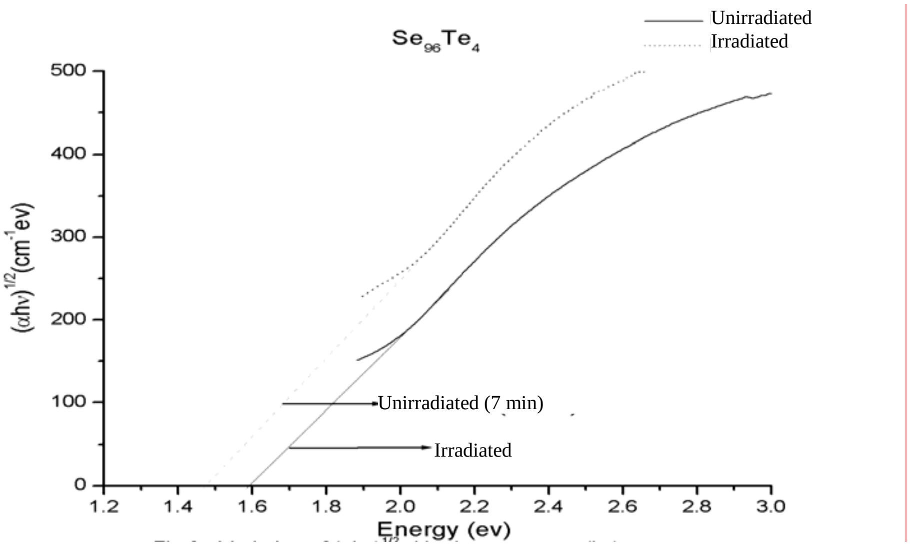

Fig. 3. Variation of $(\alpha h\nu)^{1/2}$ with photon energy ($h\nu$) for irradiated and un-irradiated $Se_{96}Te_4$ thin film.

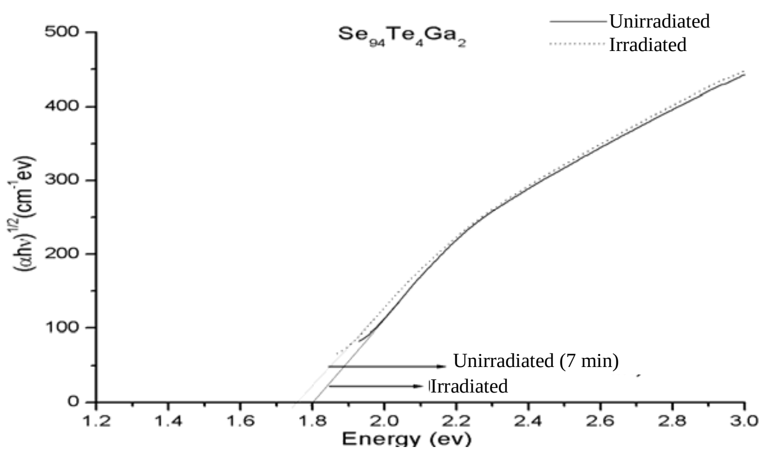

Fig. 4. Variation of (αhν)$^{1/2}$ with photon energy (hν) for irradiated and un-irradiated Se$_{94}$Te$_4$Ga$_2$ thin film.

The high-energy ions excite the electrons from the lone pair and bonding states to higher energy states. Vacancies created in these states are immediately filled by the outer electrons with Auger processes that in turn induce more holes in the lone pair and bonding orbital leading to a vacancy cascade process. In this process, bond breaking or ionization of atoms is easier to occur, which leads to a change in the local structural order of the amorphous network causing a decrease in the optical band gap. The increase in the optical band gap on the addition of Ga in the Se$_{96-x}$Te$_4$Ga$_x$ system may be explained on the basis of the model of density of states in amorphous solids proposed by Mott and Davis [15]. According to this model, the width of localized states near the mobility edges depends on the degree of disorder and defects presented in the amorphous structure. In particular, it is known that unsaturated bonds together with some saturated bonds [16] are produced as a result of insufficient number of atoms deposited in the amorphous films [17]. The unsaturated bonds are responsible for the formation of some defects in the films. Such defects produce localized states in the amorphous solids. Moreover, the increase in the optical band gap may be explained on the basis of the defects introduced in the system due to Ga incorporation. On the addition of Ga, Ga-Se bonding is developed, which introduces a larger number of defects in the system. The Ga-Se bond concentration increases with Ga concentration. It may also be due to the formation of an impurity band adjacent to a band and the formation of the tails of states extending the band into the mobility gap [18].

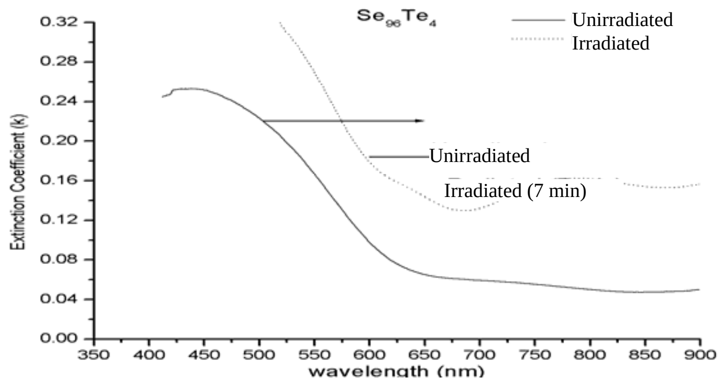

Fig. 5. Variation of Extinction Coefficient (k) with wavelength for irradiated and un-irradiated Se$_{96}$Te$_6$ thin film.

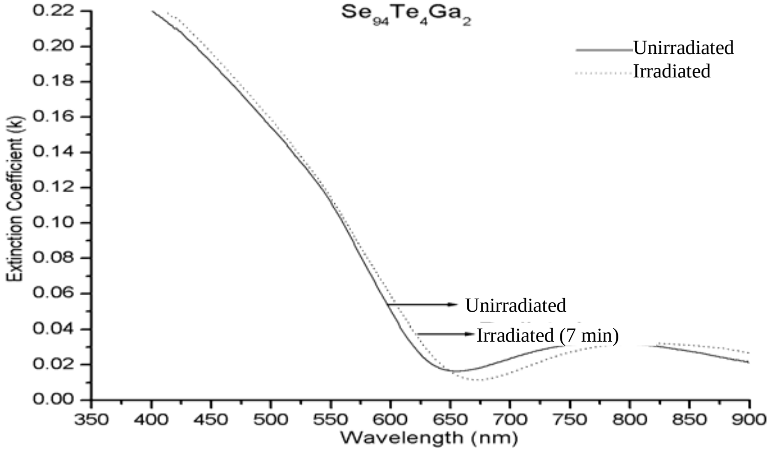

Fig. 6. Variation of Extinction Coefficient (k) with wavelength for irradiated and un-irradiated $Se_{94}Te_4Ga_2$ thin film.

Extinction coefficient k have been calculated using the well known relation [19-20]

$$\alpha = \frac{4\pi\kappa}{\lambda} \tag{3}$$

λ is the wavelength of incident beam.

The extinction coefficient (k) decreases as the Ga concentration increases, and increases after irradiation in $Se_{94-x}Te_4Ga_{x-2}$ system as shown in Figs. 5 and 6. Mott and Davis [15] have also observed a similar trend for the thin films of the various other amorphous semiconductors. The values of the extinction coefficient before and after irradiation are given in Table 1.

4. Conclusion

The optical transmission spectra of amorphous thin films of $Se_{96-x}Te_4Ga_x$ (x = 0 and 2) are obtained in the wavelength range 350-900 nm by spectrophotometer before and after irradiation in both the glassy alloys. The optical band gap (E_g) increases from (1.59-1.80 eV) with increase in Ga content in $Se_{96-x}Te_4Ga_x$ system. It is observed that optical band gap (E_g) decreases after laser irradiation. It is also observed that absorption coefficient (α) and extinction coefficient decrease with Ga content. The results have been explained on the basis of enhanced valence band tailing caused by laser irradiation and the initiation of the Auger process upon irradiation. Elliot [21] has predicted similar result from the analysis of the light irradiated chalcogenides.

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