

OPTICAL CHANGES INDUCED BY LASER-IRRADIATION ON THIN FILMS OF $\text{Se}_{75}\text{S}_{15}\text{Ag}_{10}$ CHALCOGENIDE

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Chalcogenide thin films of $\text{Se}_{75}\text{S}_{15}\text{Ag}_{10}$ have been prepared by using thermal evaporation technique with thickness of 3000 Å. Optical constants (absorption coefficient, optical band gap, refractive index and extinction coefficient) of as evaporated and laser irradiated thin films of $\text{Se}_{75}\text{S}_{15}\text{Ag}_{10}$ has been studied as a function of photon energy in the wavelength region 400-900 nm. Analysis of the optical absorption data shows that the rule of in-direct transitions predominates. It has been found that the absorption coefficient and optical band gap increases with increasing time of laser-irradiation. This change in the optical band gap may be due to the increase in the grain size and the reduction in the disorder of the system. The values of refractive index and extinction coefficient decrease by increasing time of laser-irradiation. The results are interpreted in terms of the change in concentration of localized states due to the shift in Fermi level.

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1. Introduction

Chalcogenide glasses continue to attract the attention of researchers and engineers as a very large group of interesting solids in which unusual physical and chemical phenomena are revealed. Chalcogenides are one of the most widely known families of amorphous materials which have been extensively studied for several decades because of their interesting fundamental properties and have potential applications in optical imaging, optical recording and integrated optics, microelectronics, optical communications, amplifiers, switches, fiber, memories, voltage stabilizers, display control circuits modulators, sensors, converters, grating etc. These glasses are formed by the addition of other elements such as Ag, S, As, Ge, Te, Cd, Zn etc [1-3]. Chalcogenide glasses are sensitive to the absorption of electromagnetic radiation and show a variety of photo-induced effects as a result of illumination. Several photo-induced and laser-induced phenomena are observed in amorphous chalcogenide thin films, such as photo-crystallization, photo-polymerization etc. These changes are accompanied by change in the optical constants, i.e., change in the electronic band gap, refractive index and optical absorption coefficient. Annealing and laser irradiation can affect the photo-induced changes, in particular irreversible effects occur in as-deposited chalcogenide thin films, while reversible effects occur in well-annealed chalcogenide thin films. In addition, their characteristic low vibrational energies make them very useful for doping with rare earth ions for active application and a wide range of photo-induced phenomena make them potential candidates for optoelectronic components such as photoresists, optical memories, optical interconnects and optoelectronic circuits by light patterning. Most of these applications are based on the wide variety of light-induced, laser induced and annealing effects exhibited by these materials [4-5]. The advantages of chalcogenide glass based sensors are the high chemical stability of these vitreous materials in comparison to their

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crystalline counterpart, their good long-term stability and the low detection limit [6-7]. Chalcogenides becomes very interesting in terms of multisensor systems for the simultaneous measurement of different ions in solutions. Laser irradiation to glass has been regarded as a process for spatially selected structural modification and/or crystallization in glasses. Laser induced changes in amorphous chalcogenides are an object of systematic investigations with a view to better understanding the mechanism of the phenomena taking place in them as well as their practical applications. Development of information technology demands new optical recording materials and, therefore, good knowledge of their linear optical properties is of great interest.

A lot of research work [8-13] is going on the effect of laser irradiation, annealing, ultraviolet irradiation, γ -irradiation etc on optical and electrical properties of chalcogenide thin films. Thin films of chalcogenide glasses containing silver have found application in erasable PC optical recording [13]. In view of the above, we have decided to work on the Ag containing Se-S system, which shows ionic conduction and is relatively less studied as compared to other Ag doped chalcogenide glassy systems. The aim of the present research work is to study the effect of laser irradiation on optical constants of $\text{Se}_{75}\text{S}_{15}\text{Ag}_{10}$ chalcogenide thin films. We have chosen Se because Se-based ternary chalcogenide glasses are of interest owing to their various properties like higher conductivity, higher sensitivity, greater hardness, and smaller ageing effect as compared to pure Se. We have used sulfur as an additive material with Selenium. We have doped silver in Se-S system.

2. Experimental

The quenching technique has been adopted for the preparation of $\text{Se}_{75}\text{S}_{15}\text{Ag}_{10}$ chalcogenide glasses. High purity materials (99.999 %) were weighted according to their atomic percentage and sealed in quartz ampoules with a vacuum of 10^{-5} Torr. The sealed ampoules were kept inside a furnace where the temperature was raised to 1000°C at the rate of 3 K/min. The ampoules were rocked frequently for 10 hours at maximum temperature to make the melt homogeneous. The melt was subsequently quenched in ice water. Thin films with 3000\AA thickness of $\text{Se}_{75}\text{S}_{15}\text{Ag}_{10}$ chalcogenide were prepared on glass substrates by using an Edward Coating Unit E-306. The thickness of the films was measured by using a quartz crystal monitor, Edward model FTM 7. Before the optical measurements, samples were annealed under vacuum at temperature lower than the glass transition temperature of the powdered sample measured by using non-isothermal DSC measurement at constant heating rate 10 K/min (shown in Fig. 1). The amorphous thin films were induced by pulsed TEA N2 laser (wavelength 337.1 nm, Power 100 kW, Pulse width 1 ns) for 10, 15 and 20 min. The X-ray diffraction patterns of as-prepared and laser-irradiated (20 min.) thin films of $\text{Se}_{75}\text{S}_{15}\text{Ag}_{10}$ were taken by using Philips Model PW 1710 (shown in figure 2). The absence of sharp structural peaks in as prepared films confirm the amorphous nature and the presence of sharp structural peaks in laser-irradiated films confirm the crystalline nature of the films. A JASCO, V-500, UV/VIS/NIR computerized spectrophotometer is used for measuring optical absorption and reflection. The optical absorption was measured as a function of wavelength and incident photon energy.

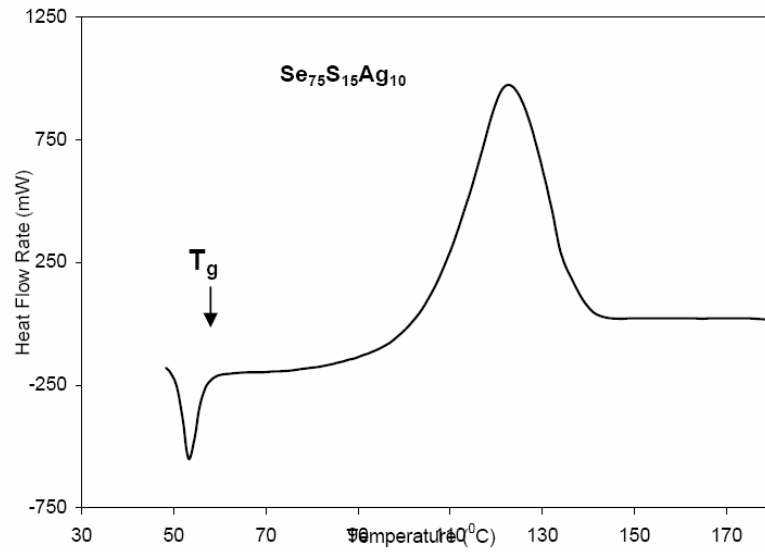


Fig. 1. DSC trace for the powdered $Se_{75}S_{15}Ag_{10}$ chalcogenide glasses at 10 K/min

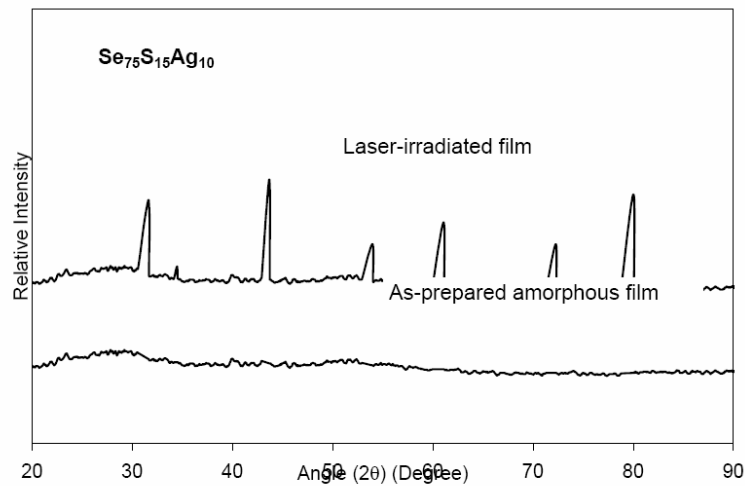


Fig. 2. X-ray diffraction pattern of amorphous films and laser-irradiated (20 min.) films of $Se_{75}S_{15}Ag_{10}$ chalcogenide glasses.

3. Results and discussion

The absorption coefficient (α) has been directly calculated from the absorbance against wavelength curves using the relation [14-17],

$$OD = \log(I_B / I_t) = \alpha t \quad (1)$$

$$\alpha = OD/t \quad (2)$$

OD is the optical density measured at a given layer thickness t (cm.). I_B and I_t are the intensities of the incident light irradiation and transmittance respectively.

The variation of the absorption coefficient (α) with different time of laser irradiation is given in table-1. It has been observed that the value of absorption coefficient (α) increases with the increase in time of laser-irradiation.

The present system of $\text{Se}_{75}\text{S}_{15}\text{Ag}_{10}$ obeys the role of non-direct transition and the relation between the optical gap (E_g), optical absorption coefficient (α) and the energy ($h\nu$) of the incident photon is given by [14-18],

$$\alpha h\nu = A(h\nu - E_g)^2 \quad (3)$$

The variation of $(\alpha h\nu)^{1/2}$ with photon energy ($h\nu$) for as deposited and laser-irradiated thin films of $\text{Se}_{75}\text{S}_{15}\text{Ag}_{10}$ are shown in Fig. 3. The value of indirect optical band gap has been calculated by taking the intercept on the X-axis. The calculated values of E_g are given in table-1. It is evident from this table that the value of optical band gap increase with increasing time of laser-irradiation. The increase in the optical band gap with increasing time of laser-irradiation may be due to the increase in grain size, the reduction in the disorder and decrease in density of defect states (which results in the reduction of tailing of bands) [19-21]. The increase in the optical band gap could also be discussed on the basis of density of state model proposed by Mott and Davis [22]. According to this model, the width of the localized states near the mobility edges depends on the degree of disorder and defects present in the amorphous structure. In particular, it is known that unsaturated bonds together with some saturated bonds are produced as the result of an insufficient number of atoms deposited in the amorphous film [23-24]. The unsaturated bonds are responsible for the formation of some of the defects in the films, producing localized states in the amorphous solids. Chalcogenide thin films always contain a high concentration of unsaturated bonds or defects. These defects are responsible for the presence of localized states in the amorphous band gap. During laser-irradiation, the unsaturated defects are gradually annealed out producing a large number of saturated bonds. The reduction in the number of unsaturated defects decreases the density of localized states in the band structure consequently increasing the optical band gap. The dependence of optical band gap with increasing time of laser-irradiation is attributed to the reduction in disorder in the atomic bonding between neighbors and thus a decrease of the density of tail states adjacent to the band edge. This increase of band gap can be attributed to the amorphous-crystalline transformations. During laser-irradiation amorphous solids got enough vibrational energy to break some of the weaker bonds, thus introducing some transnational degrees of freedom to the system. Consequently, crystallization via nucleation and growth becomes possible and depends on the time of laser-irradiation. The amount of crystalline phase increases with increasing time of laser-irradiation.

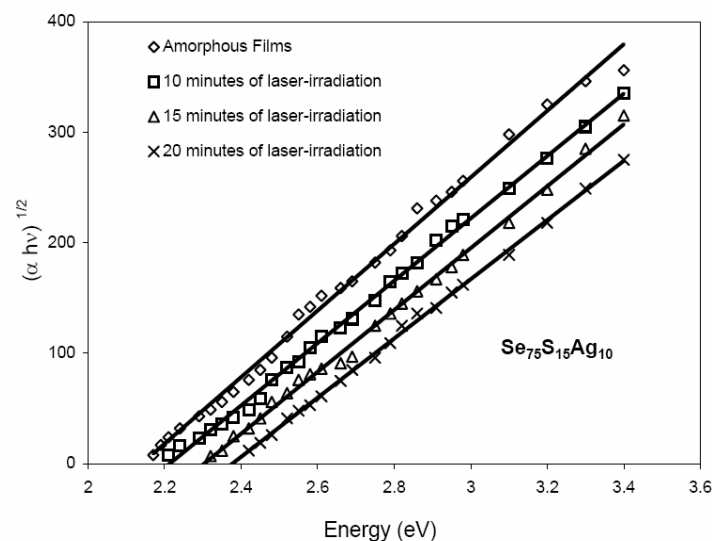


Fig. 3. $(\alpha h\nu)^{1/2}$ against photon energy for as deposited and laser-irradiated thin films of $\text{Se}_{75}\text{S}_{15}\text{Ag}_{10}$

The optical behavior of a material is generally utilized to determine its optical constants, refractive index (n) and extinction coefficient (k). Separate determinations of n and k can be made by measuring reflectance and transmittance of the same specimen. The theory for reflectance of light from a thin film is well known and is expressed in terms of Fresnel's coefficients as given by [25]

$$r_{1p} = (n_0 \cos \phi_1 - n \cos \phi_0) / (n_0 \cos \phi_1 + n \cos \phi_0) \quad (4)$$

$$r_{1s} = (n \cos \phi_0 - n_0 \cos \phi_1) / (n \cos \phi_1 + n_0 \cos \phi_0) \quad (5)$$

$$t_{1p} = 2n \cos \phi_1 / (n_0 \cos \phi_1 + n \cos \phi_0) \quad (6)$$

$$t_{1s} = 2n \cos \phi_1 / (n \cos \phi_1 + n_0 \cos \phi_0) \quad (7)$$

where n_0 and n are the refractive indices of two isotropic media. ϕ_1 is the angle of incidence of light at the interface n_0/n separating two media and ϕ_0 is the angle of refraction. r_{1p} and r_{1s} are the Fresnel's reflection coefficients for plane polarized components in which the electric vector lies parallel (p) and perpendicular (s) to the plane of incidence and t_1 is the amplitude of transmitted to incident light. Using Snell's law, we have,

$$n_0 \sin \phi_0 = n \sin \phi_1 \quad (8)$$

The reflectivity (R) of an interface can be given as

$$R_p = R_s = r_{1p}^2 = r_{1s}^2 \quad (9)$$

For normal incidence at n/n_0 interface

$$R = R_p = R_s = [(n - n_0) / (n + n_0)]^2 \quad (13)$$

For air as one medium $n_0 = 1$ and considering film as second medium which is highly absorbing in nature, the above relations can be rewritten as

$$R = \left[\frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2} \right] \quad (10)$$

Equation (10) can also be written as,

$$n = [2(1 + R) + \{4(1 + R)^2 - 4(1 - R)^2(1 + k^2)\}^{1/2}] / [2(1 - R)] \quad (11)$$

Where k is the extinction coefficient of the film and is given by,

$$k = (\alpha \lambda) / (4\pi) \quad (12)$$

Thus using relations (11) and (12), the values of refractive index (n) and extinction coefficient (k) at different incident photon energy can be calculated.

Table 1. Optical constants of amorphous and laser-irradiated thin films of $Se_{75}S_{15}Ag_{10}$ at 780 nm

Optical constants	As-deposited amorphous films	After 10 minutes of laser-irradiation on amorphous films	After 15 minutes of laser-irradiation on amorphous films	After 20 minutes of laser-irradiation on amorphous films
Absorption coefficient (α) (cm^{-1})	2.36×10^4	2.49×10^4	2.76×10^4	2.84×10^4
Optical Band Gap (E_g)(eV)	2.14	2.23	2.31	2.38
Refractive index (n)	2.88	2.54	2.08	1.89
Extinction coefficient (k)	0.137	0.121	0.098	0.073

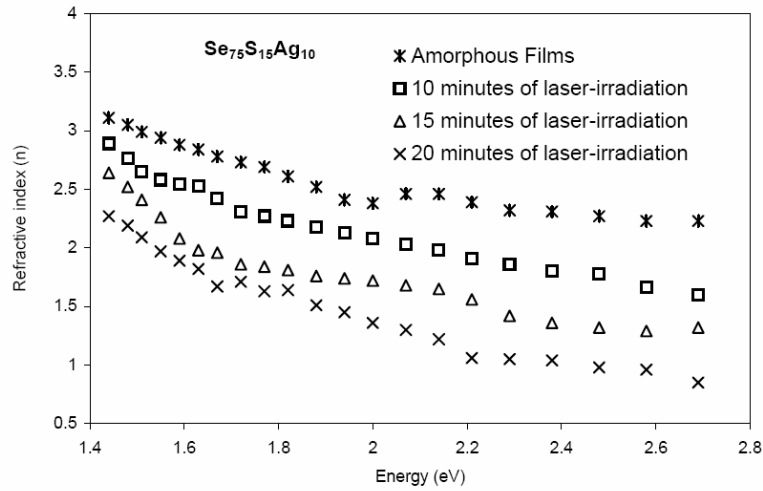


Fig. 4. Variation of refractive index (n) with incident photon energy ($h\nu$) for as deposited and laser-irradiated thin films of $\text{Se}_{75}\text{S}_{15}\text{Ag}_{10}$

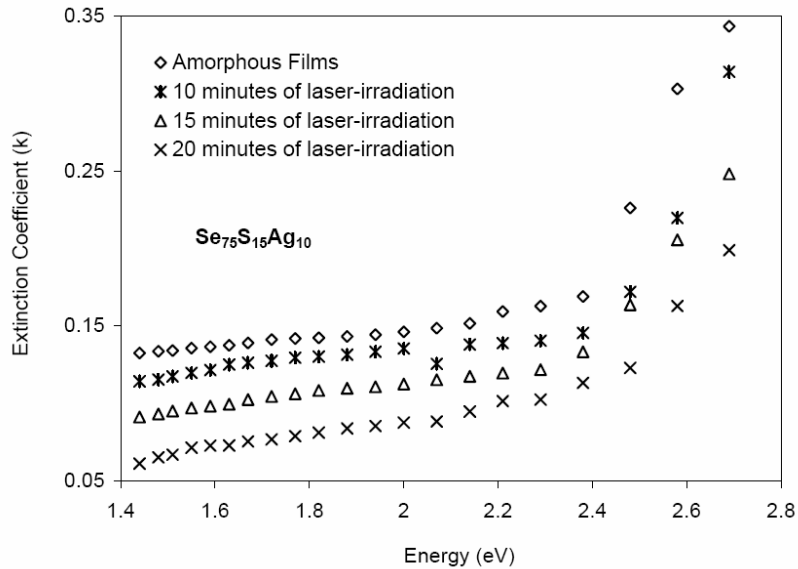


Fig. 5. Variation of extinction coefficient (k) with incident photon energy ($h\nu$) for as deposited and laser-irradiated thin films of $\text{Se}_{75}\text{S}_{15}\text{Ag}_{10}$

The spectral dependence of refractive index and extinction coefficient for as deposited and laser-irradiated thin films of $\text{Se}_{75}\text{S}_{15}\text{Ag}_{10}$ are shown in Fig. 4 and Fig. 5. The value of refractive index decreases while the value of extinction coefficient increases with increasing the photon energy. The values of n and k for different time of laser-irradiation are shown in table 1. It is clear from this table that n and k both decrease with increasing time of laser-irradiation, which can be explained as, chalcogenide thin films always contain a high concentration of unsaturated bonds or defects. These defects are responsible for the presence of localized states in the amorphous band gap. During laser-irradiation, the unsaturated defects are gradually annealed out producing a large number of saturated bonds. The reduction in the number of unsaturated defects decreases the density of localized states in the band structure consequently decreasing the refractive index and extinction coefficient.

4. Conclusions

In this work, the effect of laser-irradiation on the optical constants of chalcogenide thin films of $\text{Se}_{75}\text{S}_{15}\text{Ag}_{10}$ was measured in the wavelength region 400-900 nm. It has been found that the optical band gap increases on increasing the time of laser-irradiation. This may be due to the increase in the grain size, the reduction in the disorderedness of the system. This may also be due to the decrease in the density of defect states, which results in the reduction of tailing of bands. After laser irradiation on amorphous films the optical band gap increases, which shows that the amorphous films became crystallized. The refractive index and extinction coefficient decreases with increasing time of laser-irradiation. The change in refractive index of these materials under the influence of light enables and laser-irradiation shows that these materials can be used in optical data storage and other devices.

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