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γ-Irradiation effects on the optical properties of amorphous $Ge_{10}As_{30}Se_{60}$ thin films

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ABSTRACT

Amorphous $Ge_{10}As_{30}Se_{60}$ thin films on glass substrates were prepared by thermal evaporation method. The effect of γ-irradiation on the optical properties of the amorphous $Ge_{10}As_{30}Se_{60}$ thin films was studied in the spectral range from 200 nm to 1100 nm. γ-Radiation-induced bleaching was observed after irradiation of the samples for doses up to 50 kGy. An increase in transmission and a shift in the (transmission) absorption edge towards higher energies were observed with the irradiation dose. An increase in the optical energy gap with irradiation dose was also observed in the studied range. Photo-bleaching due to γ-irradiation was discussed in light of the structural aspects and configurational-coordinate model for Ge–As–Se.

1. Introduction

Amorphous chalcogenide semiconductors are of interest for many applications such as in infrared technology, modern telecommunications systems and nonlinear optics [1,2]. They are characterized by their sensitivity to the influence of external factors especially ionizing radiation [3–5]. It is well known that the optical properties of amorphous chalcogenide semiconductors are determined by the coordination defect concentration. When amorphous chalcogenides are irradiated, bond breaking and bond rearrangement can take place, resulting in changes of the local structure of these materials. These include subtle effects such as shifts in the absorption edge (photo-bleaching and photo-darkening), and more substantial atomic and molecular reconfiguration. In general, these phenomena are associated with the changes in the optical constants and absorption edge shift [6], allowing the use of these materials in the fabrication of a large number of optical devices. This clearly underlines the importance of these chalcogenide materials by accurate determination of their optical constants, refractive index, extinction coefficient and the optical band gap. Alloying chalcogenide glassy semiconductors with Ge is an effective way of controlling the electrical and optical properties of glasses in a desired direction. In the GeAsSe amorphous system, at low Ge content the glasses have a characteristic layer structure dominated by the presence of pyramids of $AsSe_{3/2}$ and $GeSe_{3/2}$. As the Ge content increases, the glass develops a more three dimensional network dominated by Ge–Se bonds. The properties of the amorphous GeAsSe system can be correlated with structure characterized by the average coordination number $\langle r\rangle$, calculated using

$$\langle r\rangle = \frac{\alpha N_{Ge} + \beta N_{As} + \gamma N_{Se}}{\alpha + \beta + \gamma} \quad (1)$$

where, α, β, γ and N_{Ge}, N_{As}, N_{Se} are the ratios and average coordination numbers of Ge, As and Se, respectively. From this equation, the average coordination number of the composition under investigation was found to be 2.5. Using this measure, compositions in the amorphous GeAsSe system with low $\langle r\rangle$ are generally over-stoichiometric in Se and are characterized by having a "floppy" glass network containing large numbers of Se–Se chains or rings; while those with the highest $\langle r\rangle$ generally are over-stoichiometric in Ge and will contain large numbers of homopolar (Ge–Ge) or defect bonds (Ge–As). The so-called intermediate phase amorphous compositions with $\langle r\rangle$ around 2.4–2.5 in this system display some unique physical properties including a near absence of the latent heat of melting. This means that the glass configuration in the solid is the same as that in the corresponding molten phase. This intermediate phase results in stress-free but rigid glass networks [7]. This work deals with the study of the γ-radiation-induced effect on the optical properties of the ternary amorphous $Ge_{10}As_{30}Se_{60}$ composition.

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2. Experimental

Amorphous $Ge_{10}As_{30}Se_{60}$ composition was prepared by the melt quenching technique from Se, As and Ge of 5 N purity. The appropriate amounts of elements were placed in a clean dry silica ampoule and then sealed under a vacuum of 10^{-4} torr. The ampoule was then heated up in steps up to a temperature of 900 °C and kept at this temperature for 20 h. The ampoule was then quenched in an ice-water mixture to obtain the amorphous material ingots. The prepared ingots were confirmed to be completely amorphous using X-ray diffraction. Thin films of $Ge_{10}As_{30}Se_{60}$ were grown by thermal evaporation method, on glass substrates kept at room temperature using an Edwards E-306 Coating unit under a pressure in the order of 10^{-5} torr. Film growth rate and thickness was monitored during growth using a quartz crystal thickness monitor. The amorphous nature of the grown films was confirmed using X-ray diffractometer, type Shimadzu XD-D series. Films were confirmed to have the same composition as the bulk material using an EDX unit attached to Joel SEM. Optical measurements were carried out at room temperature in the spectral range from 200 nm to 1100 nm using UV/VIS Shimadzu 160A spectrophotometer. γ-Irradiation for different doses was carried out in the cavity of a ^{60}Co γ-irradiator. The dose rate was 5 kGy/h and the temperature of the irradiation cavity was lower than 320 K.

3. Results and discussion

The variation of the absorption coefficient of $Ge_{10}As_{30}Se_{60}$ thin films with incident photon energy for three γ-irradiation doses is shown in Fig. 1. The absorption coefficient was calculated from the absorbance spectra as well as from the transmittance and reflectance spectra of the $Ge_{10}As_{30}Se_{60}$ film. The calculated values of the absorption coefficient in both cases were nearly identical within ±2%. From Fig. 1, it can be noticed that the absorption coefficient decreases with irradiation dose in the shown range. Also, the absorption edge shifts towards higher energies with the increase of irradiation dose; this is called blue shift of the absorption edge. It can be noticed that the absorption edge region extends more into the higher energy side with increasing irradiation dose. Also, saturation for the non-irradiated sample starts at energy 2.43 eV while for the 15 kGy and 50 kGy irradiated samples it starts at 2.53 eV and 3 eV, respectively. This could be correlated to the local structural changes occurring as a result of irradiation.

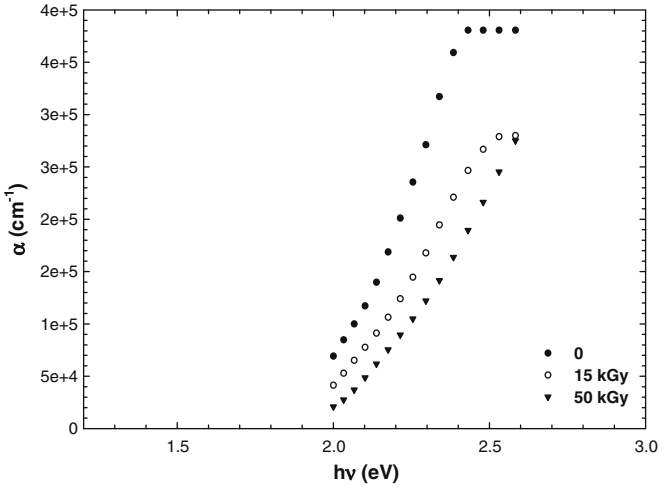

Fig. 1. The variation of the absorption coefficient with photon energy for as-deposited and some irradiated samples.

As the dose increases, the resulting structural changes, such as bond angle and length variations, lead to an increase in the absorption edge region. The absorption coefficient, α, in the high absorption region, assuming parabolic valence and conduction band edges, is given by [8]

$$\alpha(h\nu) = B(h\nu - E_g)^2/h\nu \quad (2)$$

where, E_g is the optical energy gap, the parameter B is given by the slope of the plots of $(\alpha h\nu)^{1/2}$ vs $h\nu$, is an interesting parameter, since it can be taken as a measure of the disorder. The optical energy gap, E_g, is determined from the intersection of the plot $(\alpha h\nu)^{1/2}$ vs $h\nu$ with the abscissa axis as shown in Fig. 2. The optical energy gap values were found to increase with irradiation dose. It increases from 1.73 eV for the un-irradiated sample to 1.8 eV after 50 kGy of γ-irradiation. The variation of the optical energy gap, E_g, with the γ-irradiation dose is shown in Fig. 3. E_g has a nearly linear dependence on the irradiation dose, in the studied range. The change in the optical energy gap with irradiation may be related to structural changes that can lead to change in the density of localized states. Bond breaking, bond angle variations and bond rearrangement of atoms can take place upon irradiation of chalcogenide glasses; this can result in the change in local structure order of the amorphous network [9,10]. As mentioned in the introduction, the GeAsSe

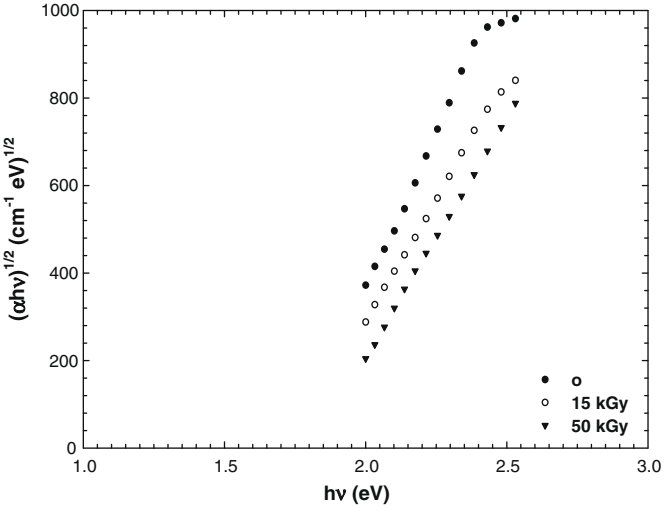

Fig. 2. The variation of $(\alpha h\nu)^{1/2}$ with the incident photon energy for as-deposited and some irradiated samples.

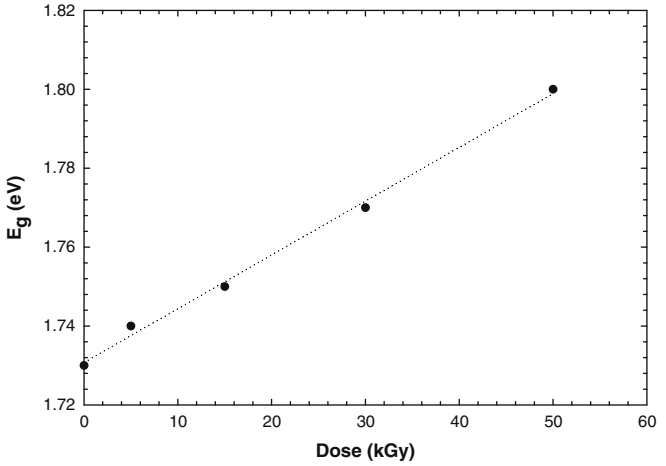

Fig. 3. The nearly linear change of optical energy gap with irradiation dose.