Hindawi Publishing Corporation
Research Letters in Materials Science
Volume 2008, Article ID 826402, 4 pages
doi:10.1155/2008/826402

Research Letter

Effect of Ge Addition on the Optical Band Gap and Refractive Index of Thermally Evaporated As_2Se_3 Thin Films

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Received 18 October 2007; Accepted 26 February 2008

Recommended by Maria Loi

The present paper reports the effect of Ge addition on the optical band gap and refractive index of As_2Se_3 thin films. Thin films of As_2Se_3 and $(As_2Se_3)_{90}Ge_{10}$ were prepared by thermal evaporation technique at base pressure 10^{-4} Pa. Optical band gap and refractive index were calculated by analyzing the transmission spectrum in the spectral range 400–1500 nm. The optical band gap decreases while the refractive index increases with the addition of Ge to As_2Se_3. The decrease of optical band gap has been explained on the basis of density of states; and the increase in refractive index has been explained on the basis increase in disorder in the system.

1. INTRODUCTION

Chalcogenide glasses based on the chalcogen elements S, Se, and Te are attractive and widely investigated materials as they possess high optical transparency in the IR region. They have low phonon energy, high photosensitivity, easy fabrication and processing, and good chemical durability. So they are used in ultrafast optical switches, frequency converters, optical amplifiers, optical recording devices, integrated optics, infrared lasers, and infrared transmitting optical fibres [1–3]. Chalcogenide semiconducting alloys have found application not only due to their electrical and thermal properties, but also due to their optical properties. Many amorphous semiconducting glasses, in particular selenium, exhibit a unique property of reversible transformation. Its various device applications like rectifiers, photocells, xerography, switching and memory, and so on have made it attractive, but pure selenium has disadvantages like short lifetime and low sensitivity. Due to high glass-forming ability of Se, it represents a good host matrix for the investigation of chalcogenide glasses in the bulk and thin film forms [4–7]. Thus, the above problems can be overcome by alloying Se with some impurity atoms (Bi, Te, Ge, Ga, As, etc.), which gives higher sensitivity, higher crystallization temperature, and smaller ageing effects [8–10]. The As-Se-Ge system has been extensively studied [11–13] because of the fact that Ge, As, and Se are the elements of same period in groups IV-VI, and it brings about the covalent character of the interaction between their atoms. This results in a broad glass formation region in As-Se-Ge system [14] among all investigated three-component chalcogenide systems.

The present work reports the effect of Ge addition on the optical band gap and refractive index of arsenic selenide thin films. The straightforward technique proposed by Swanepoel has been used for analyzing the transmission spectra in the spectral range 400–1500 nm [15].

2. EXPERIMENTAL PROCEDURE

Two compositions of $(As_2Se_3)_{100-x}Ge_x$ ($x = 0, 10$) chalcogenide system were prepared using melt quench technique. The materials (5 N pure) were sealed in evacuated ($\sim 10^{-4}$ Pa) quartz ampoules each of 3 g batch, weighed according to their atomic weight percentage. The sealed ampoules were kept inside a furnace where the temperature was increased up to 950°C in five steps (200°C, 400°C, 600°C, 950°C) gradually at a heating rate of 2-3°C/min. The ampoules were frequently rocked for 24 hours at the highest temperature to make the melt homogeneous. The quenching was done in ice cold water. Thin films were prepared on cleaned glass substrates (microscopic glass slides). The substrates were cleaned with soap solution, ultrasonically cleaned by trichloroethylene, acetone followed by methyl alcohol. In last, the substrates were washed by DI water and dried in oven at approximately 110°C. Thin films of the alloys were prepared by thermal evaporation technique (Vacuum coating unit HINDVAC 12A4D Model) at room temperature and base pressure of $\sim 10^{-4}$ Pa using a molybdenum boat. The thickness of the deposited thin films has been measured by thickness monitor (DTM-101). The compositions of evaporated samples have been measured by an electron microprobe analyzer (JEOL 8600 MX) on different spots (size $\sim$ 2 μm). For the composition analysis, the constitutional elements (As, Se, and Ge) and the bulk original alloys, that is, $(As_2Se_3)_{100-x}Ge_x$, are taken as reference samples. The composition of 2×2 cm^2 sample is uniform within the measurement accuracy of about ±0.2%. Amorphous nature of the bulk samples and thin films was checked by XRD technique. No prominent peak is observed in the bulk as well as in thin films. The normal incidence transmission spectra of $(As_2Se_3)_{100-x}Ge_x$ thin films were obtained by a double beam ultraviolet-visible-near infrared spectrophotometer [Hitachi-330], in the transmission range 400–1500 nm. The spectrophotometer was set with a suitable slit width of 1 nm in the measured spectral range. All optical measurements were performed at room temperature (300 K).

3. RESULTS AND DISCUSSION

Optical transmission (T) is a very complex function and is strongly dependent on the absorption coefficient (α). Figure 1 shows the variation of transmission (T) with wavelength (λ) in As_2Se_3 and $(As_2Se_3)_{90}Ge_{10}$ thin films. According to Swanepoel's method [15], the envelope of the interference maxima and minima of transmission spectra can be used for deducing optical parameters. The refractive index (n) of the thin films is obtained by the envelope method by making use of the following expressions. In the transparent region where the absorption coefficient $\alpha \approx 0$, the refractive index (n) is given by

$$n = \left[N + \left(N^2 - s^2\right)^{1/2}\right]^{1/2}, \qquad (1)$$

where

$$N = \frac{2s}{T_m} - \frac{(s^2+1)}{2} \qquad (2)$$

and T_m is the envelope function of minimum transmittance, and s is the refractive index of substrate. In the weak region, where absorption coefficient $\alpha \neq 0$, the transmittance decreases due to the influence of α, the value of N in (1) is given by

$$N = 2s\frac{T_M - T_m}{T_M T_m} + \frac{(s^2+1)}{2}, \qquad (3)$$

and T_m is the envelope function of maximum transmittance.

The extinction coefficient (k) can be calculated using the relation $k = (\lambda/4\pi d)\ln(1/x)$, where d is the thickness of the film and x is the absorbance [15]. If n_1 and n_2 are the refractive indices of two adjacent maxima or minima at wavelengths λ_1 and λ_2, then the thickness of the film is given by $d = \lambda_1\lambda_2/2(\lambda_1 n_2 - \lambda_2 n_1)$. The thickness of the thin films calculated using the above relation is given in Table 1 and found to be within ±35 nm with thickness values measured while depositing the thin films using thickness monitor.

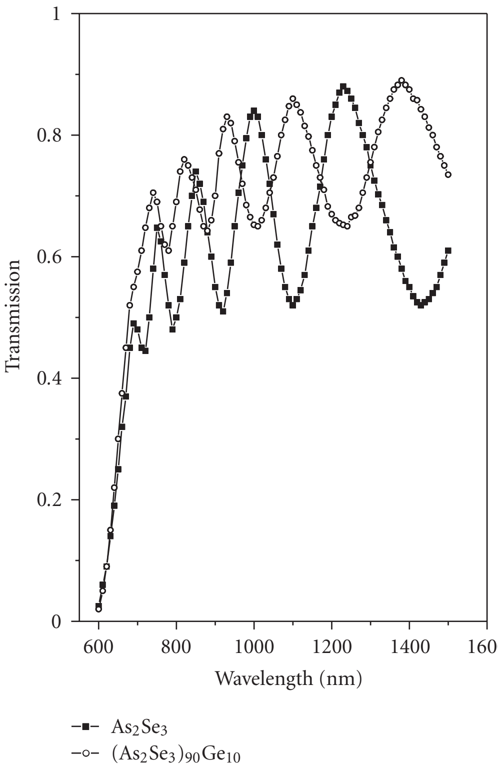

FIGURE 1: Transmission spectrum for As_2Se_3 and $(As_2Se_3)_{90}Ge_{10}$ thin films.

TABLE 1: Values of thickness (d), n, k, and E_g^{opt} for As_2Se_3 and $(As_2Se_3)_{90}Ge_{10}$ thin films.

Composition	d (nm)	at 800 nm		E_g^{opt} (eV)
		n	k	
As_2Se_3	934	2.50	0.0054	1.52
$(As_2Se_3)_{90}Ge_{10}$	900	2.64	0.0076	1.46

The variation of refractive index (n) and extinction coefficient (k) with wavelength is shown in Figures 2 and 3, respectively. From figures, it is clear that both refractive index and extinction coefficient decrease with the increase of wavelength for the thin films under study. The decrease in the value of refractive index with wavelength shows the normal dispersion behavior of the material. On the part of Ge addition to As_2Se_3 thin films, the refractive index has been found to have higher values. This increase in the refractive index may be ascribed to increase of disorder in the structure, change in stoichiometry and internal strain caused with the addition of Ge. The values of n and k at 800 nm (as nearly at this wavelength the spectrum region changes) are given in Table 1.

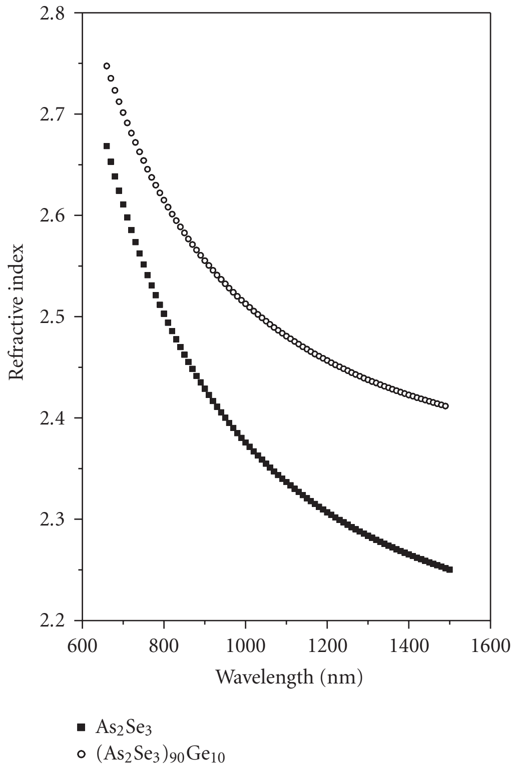

FIGURE 2: Plot of refractive index versus wavelength for As_2Se_3 and $(As_2Se_3)_{90}Ge_{10}$ thin films.

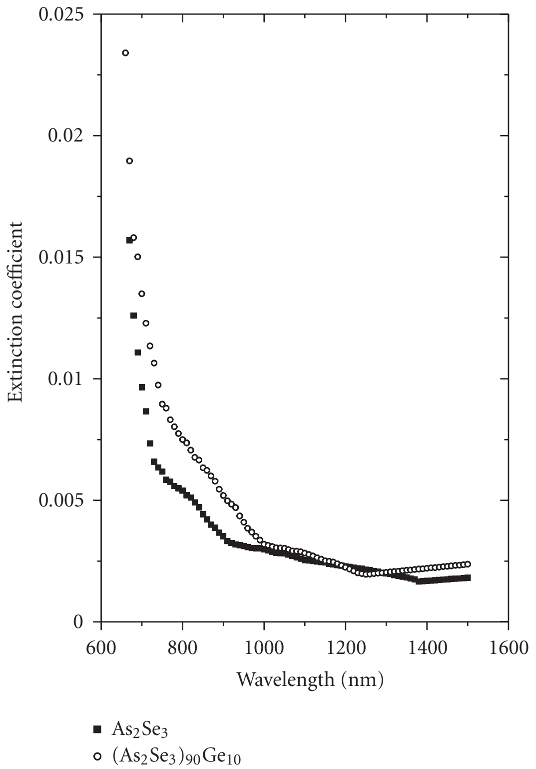

FIGURE 3: Plot of extinction coefficient versus wavelength for As_2Se_3 and $(As_2Se_3)_{90}Ge_{10}$ thin films.

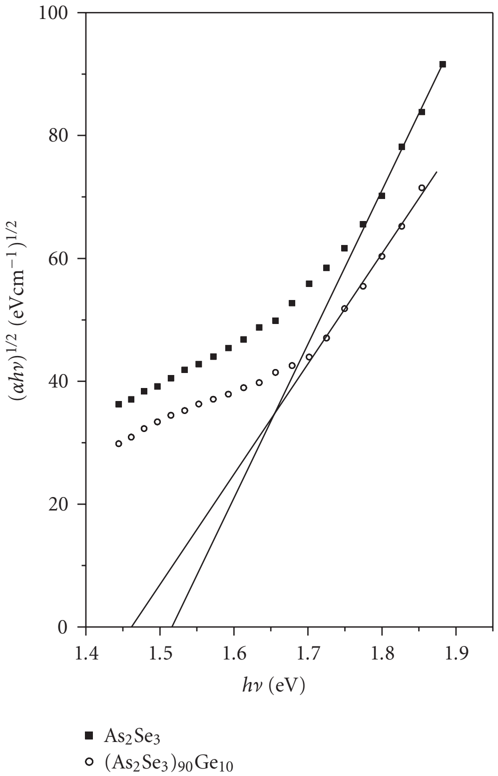

FIGURE 4: Plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for As_2Se_3 and $(As_2Se_3)_{90}Ge_{10}$ thin films.

The optical band gap (E_g^{opt}) has been determined from absorption coefficient data as a function of photon energy, according to the generally accepted "nondirect transition" model for amorphous semiconductors [16], proposed by Tauc [17] $\alpha h\nu = B(h\nu - E_g^{opt})^n$, where $h\nu$ is the photon energy, α is the absorption coefficient, E_g^{opt} the optical band gap, B is band tailing parameter, and $n = 1/2$ for direct band gap and $n = 2$ for indirect band gap. Figure 4 shows the variation of $(\alpha h\nu)^{1/2}$ with $h\nu$. Optical band gap can be determined by the extrapolation of best-fit line between $(\alpha h\nu)^{1/2}$ and $h\nu$ to intercept the $h\nu$ axis $(\alpha = 0)$ for thin films. The region of the transparency is limited by an intrinsic absorption at short and long wavelengths, the position at short wavelength corresponds to $\lambda = hc/E_g$, where λ is wavelength, h is Planck's constant, c is light velocity, and E_g is energy width of the forbidden band [18]. So best-fit line between $(\alpha h\nu)^{1/2}$ and $h\nu$ to intercept the $h\nu$ axis $(\alpha = 0)$ is taken only for short wavelengths, that is, where absorption is strong. It is found that the optical band gap decreases with the addition of Ge to As_2Se_3 thin films. The variation in optical parameters with Ge incorporation is mainly due to change in stoichiometry. The Ge additive in As_2Se_3 must bring about a compositional change of host network of As-Se. In the fundamental absorption region, the absorption is due to the transition from the top of valence band to the bottom of the conduction band. Addition of Ge in As_2Se_3 thin film may cause an increase in the density of state-in-the-valence band. The addition of Ge may also create localized states in the band gap [19]. This will lead to a shift in the absorption edge towards lower photon energy, and, consequently, the decrease in the optical energy gap can be explained by the increased tailing [20] of the conduction band edge into the gap due to the addition of germanium impurities.

4. CONCLUSION

The thermally evaporated thin films of the As_2Se_3 as well as $(As_2Se_3)_{90}Ge_{10}$ were analyzed using their transmission spectra in the spectral range 400–1500 nm. The optical parameters viz. n, k, and E_g^{opt} were calculated. Refractive index and extinction coefficient were found to increase while optical band gap decreases with Ge addition to As_2Se_3. The increase in the refractive index with the addition of Ge has been explained on the basis of the increase in disorder in the system. The decrease in optical band gap with Ge addition has been explained on the basis of density of states.

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