

Spectroscopic ellipsometry study of amorphous GeSe thin films doped with Cd and Te

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Amorphous compositions of the system $(\text{Ge}_1\text{Se}_9)_{85}\text{A}_{15}$, where A is Cd or Te, were prepared in bulk form by melt quenching technique. Thin films of the bulk compositions were grown on glass substrates by thermal evaporation. The effect of Cd or Te addition on some optical parameters of Ge_1Se_9 was investigated in the spectral range from 300 nm to 650 nm using spectroscopic ellipsometry (SE) technique. The refractive index was found to decrease, in general, with increasing incident photon energy while the extinction coefficient was found to increase. Addition of Cd causes decrease of the refractive index while addition of Te causes its increase. The real and imaginary parts of the complex refractive index were calculated for compositions under investigation and discussed in reference to the energy band structure of the studied semiconducting materials.

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1. Introduction

Chalcogenides have drawn great attention because of their potential applications in various solid-state and optoelectronic devices. They are also well known as IR transmitting materials [1] having pass bands from visible to beyond 15 μm (depending on composition). Chalcogenide glasses are characterized by a high density of localized states with the absence of spin paramagnetism. This is associated with the presence of a pinned Fermi level and the absence of unpaired electrons, in which the concept of charged defects D^+ , D^- , D^0 is considered. Such a concept was suggested by Street and Mott [2-4] and found various practical applications. Chalcogenides are known to have flexible structure in the sense that each atom can adjust its neighboring environment to satisfy the valence requirements [5]. Ge-based ternary chalcogenide amorphous semiconductors have found many potential applications in a variety of fields. Due to the tunability of the band gap energy of $(\text{Ge}_1\text{Se}_9)_{85}\text{A}_{15}$, where A is a metallic additive, this alloy can be utilized in optoelectronic devices, such as optical windows, photodetectors and optical memory devices [6, 7]. Recently, spectroscopic ellipsometry has been used to monitor changes in the optical properties in a non-destructive manner [8, 9]. Spectroscopic ellipsometry, SE, technique is a very powerful tool to characterize the surfaces of materials due to its sensitivity to modifications of the refractive index of surfaces. This sensitivity allows us to determine the optical parameters with a very high precision [10, 11]. SE is very sensitive to surface irregularities such as surface roughness, inter-diffusion and interlayer formation in multilayer thin film systems [12]. In ellipsometry, one deals with the measurement of the relative changes in the amplitude and phase of linearly polarized monochromatic light incident upon an oblique reflection from the sample surface. Experimentally, to

measure ellipsometry parameters ($\tan \psi$ and $\cos \Delta$), which are related to the optical and structural properties of the sample, are defined by:

$$\rho = \frac{R_p}{R_s} = \tan(\psi) e^{i\Delta} \quad (1)$$

where, ρ is the complex reflectance ratio, $R_p(R_s)$ is the complex reflection coefficient of the light polarized parallel (perpendicular) to the plane of incidence. The two parameters obtained in an ellipsometric measurement are ψ and Δ . From Eq. (1), ψ and Δ can be defined, respectively, by the ratio of the amplitudes of the reflection coefficients for the p and s polarized radiation and by the difference in phase between the p and s polarized components of the radiation:

$$\tan(\psi) = \frac{R_p}{R_s}, \quad \Delta = \delta_p - \delta_s \quad (2)$$

The complex refractive index of the film is given by:

$$N(\lambda) = n(\lambda) + ik(\lambda) \quad (3)$$

and the dielectric function is given by:

$$\varepsilon(\lambda) = \varepsilon'(\lambda) + i\varepsilon''(\lambda) \quad (4)$$

where, ε' is the volume polarization term for induced dipoles and ε'' is the volume absorption related to carrier generation. This paper deals with the study of the effect of addition of Cd or Te on some optical properties of the Ge_1Se_9 amorphous composition.

2. Experimental

Ge_1Se_9 amorphous composition was synthesized from high purity (5N) elements by melt quenching technique. The required ratios of the constituent elements were

introduced into clean and dry silica ampoules, which were then evacuated and sealed under vacuum of 10^{-5} torr. Synthesis of the bulk materials was carried out in a high temperature furnace. A maximum temperature of 1000K was achieved by step-wise heating and was maintained for 24 hours. The ampoule was quenched in ice-water mixture to avoid any possible crystallization upon solidification. The elements Cd and Te were added to the binary Ge_1Se_9 composition in the required ratios using the same technique. Thin films were deposited onto optically plane glass substrates by thermal evaporation using an Edwards E306 coating unit under a residual pressure of 2×10^{-6} torr. The substrates were kept at room temperature during deposition process. A quartz crystal thickness monitor was used to monitor the film thickness during film deposition. The deposition rate was maintained as low as 10 \AA/s during growth to avoid differential evaporation of the constituent elements. The growth process produced films with thickness of 1000 \AA . The deposited films were confirmed to be amorphous by the XRD technique using a Shimadzu XD-D series x-ray diffractometer. Composition of the grown films was confirmed to have the required composition using an EDX (energy dispersive X-ray) unit attached to a Joel TEM. Ellipsometric measurements were carried out at an angle of incidence 70° in the photon energy range of 1.9 eV to 4.5 eV with intervals of 0.02 eV, using a computer-controlled variable angle spectroscopic ellipsometer, VASE, of the rotating analyzer type from J.A. Woollam Company. The accuracy of the angle of incidence was $\pm 0.005^\circ$. For an instrument of the type as used in this experiment, the quantities measured are $\tan\psi$ and $\cos\Delta$, from which ellipsometric azimuths ψ and Δ are obtained. These parameters are employed to find the refractive index (n), extinction coefficient (k) and the thickness (d) of thin films, by comparison with theoretical computer-calculated spectra of the films having given values of refraction index, extinction coefficient and thickness of the thin films. A model for the optical structure of the sample is constructed after data are acquired covering the desired spectral range and angles of incidence. The Fresnel equations with the assumed model are then used to predict the expected ψ and Δ data for the wavelength, and angles of incidence chosen. Data fitting is then applied by adjusting the model parameters to find the best-fit values. The Marquardt–Levenberg algorithm is most commonly used to quickly determine the model that

exhibits the smallest difference between the measured and calculated values [13]. The difference is quantified by using mean squared error (MSE) as defined by:

$$MSE = \frac{1}{2N - M} \sum_{i=1}^N \left[\left\{ \frac{\tan \psi_i^{Mod} - \tan \psi_i^{Exp}}{\sigma_{\psi,i}^{Exp}} \right\}^2 - \left\{ \frac{\cos \Delta_i^{Mod} - \cos \Delta_i^{Exp}}{\sigma_{\Delta,i}^{Exp}} \right\}^2 \right] \quad (5)$$

where, N is the number of ψ - Δ pairs, and M is the number of variable parameters used in the model.

3. Results and discussion

XRD patterns of the as-deposited thin films are shown in figure (1), no sharp peaks characteristic to the crystalline phase were detected and hence confirming amorphous nature.

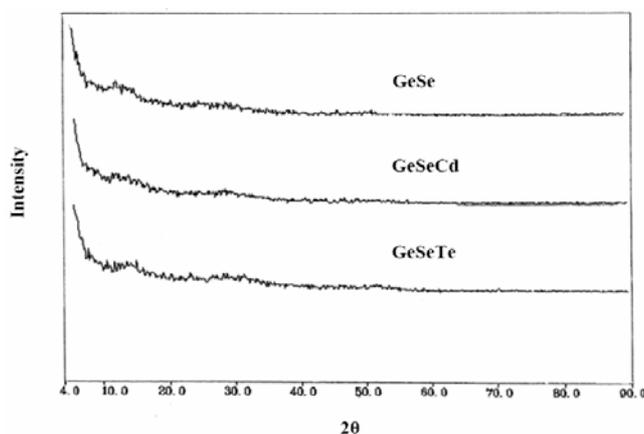


Fig. 1. The XRD patterns for the compositions under investigation.

There are some physical parameters that are related to the chemical and physical character of the studied compositions, namely, density, molar volume, the average coordination number and the number of bonds per unit volume of the prepared compositions were calculated and listed in Table 1.

Table 1. values of the energy gap, density, molar volume and the average coordination number for the studied compositions.

| Composition | E_g (eV) | $E_{g(2)}$ (eV) | Density (gcm^{-3}) | Molar Volume (cm^3) | $\langle r \rangle$ | N_b |
|---|------------|-----------------|-------------------------------|--------------------------------|---------------------|----------------------|
| $\text{Ge}_{10}\text{Se}_{90}$ | 1.8 | 1.84 | 4.85 | 16.15 | 2.2 | 8.2×10^{22} |
| $(\text{Ge}_{10}\text{Se}_{90})_{85}\text{Te}_{15}$ | 1.5 | 1.64 | 5.06 | 19.94 | 2.32 | 7.2×10^{22} |
| $(\text{Ge}_{10}\text{Se}_{90})_{85}\text{Cd}_{15}$ | 1.7 | 1.78 | 5.42 | 15.4 | 2.17 | 8.5×10^{22} |

It can be noticed that there is an increase in the density of Ge_1Se_9 with the addition of any of Cd or Te. This is due to the fact that the density of Cd (8.65 gcm^{-3})

or Te (6.24 gcm^{-3}) is greater than that of Ge (5.32 gcm^{-3}) and Se (4.8 gcm^{-3}). The molar volume of Ge_1Se_9 , listed in table (1), increases with the addition of

Te and decreases with the addition of Cd. The same behaviour was also noticed for the average coordination number. The average coordination number of elements used in calculations of $\langle r \rangle$, were 4, 2, 3, 2 for Ge, Se, Te, Cd respectively. The calculated values of the average coordination number, $\langle r \rangle$, indicate that all the compositions under study have $\langle r \rangle < 2.4$, hence having floppy or spongy glass network and are assumed to be undercoordinated [13]. The addition of Cd or Te caused no change to the type of the glass network of Ge_1Se_9 . The coordination number is less than 2.4; this is the threshold value for transition of the glass network from floppy to rigid network. Referring to table (1), one can notice that addition of Te leads to the decrease of the number of bonds per unit volume while the addition of Cd leads its increase. This may be related to the large molar volume and density of $(\text{Ge}_1\text{Se}_9)_{85}\text{Te}_{15}$ in comparison with those of $(\text{Ge}_1\text{Se}_9)_{85}\text{Cd}_{15}$. From SE measurements the refractive index, n , and the extinction coefficient, k , of the films could be determined as explained in the previous section. Figure (2), shows the variation of the refractive index with the incident photon energy for all compositions.

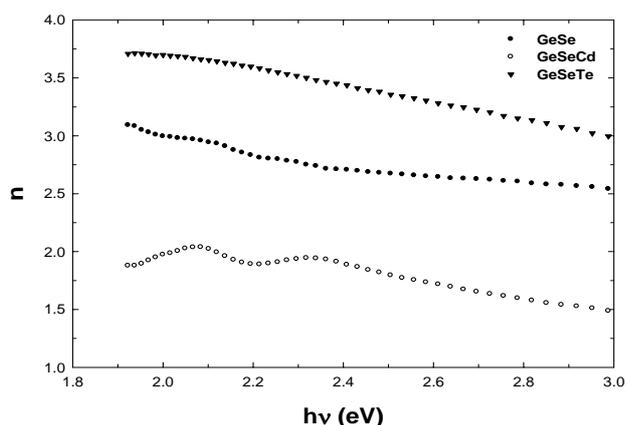


Fig. 2. The variation of the refractive index with the incident photon energy.

As clear from the figure, the refractive index of each composition tends to decrease with the incident photon energy. It is also clear that, in general, at any photon energy, the addition of Cd to Ge_1Se_9 causes the decrease of the refractive index, while the addition of Te causes the increase of the refractive index. This is not expected as the density of bulk $(\text{Ge}_1\text{Se}_9)_{85}\text{Cd}_{15}$ is higher than that of $(\text{Ge}_1\text{Se}_9)_{85}\text{Te}_{15}$ which leads to higher refractive index for the more dense bulk material. In thin film, the situation might differ due to factors such as film thickness effect, changes of bonding configuration during evaporation and film formation process. Also, this could be attributed the difference in the chemical character of the two elements. More over the above results may be correlated to the average coordination number, $\langle r \rangle$, which decreases with the addition of Cd and increases with the addition of Te.

The decrease of $\langle r \rangle$ with Cd could be explained as a tendency to have a floppy glass network and the increase of $\langle r \rangle$ towards the threshold value may mean the tendency to form a rigid glass network with Te addition. These results are in agreement with the results of ref. [14], where the refractive index and the average coordination number were found to increase with the addition of Te. The variation of extinction coefficient for all compositions with the incident photon energy is shown in Fig. (3).

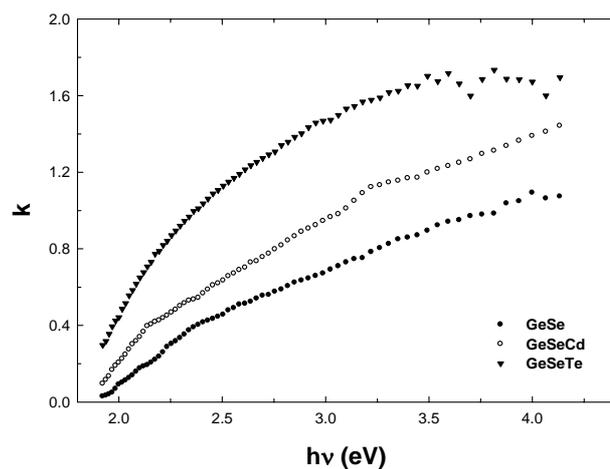


Fig. 3. the variation of the extinction coefficient with the incident photon energy.

An increase in extinction coefficient, k , with photon energy is observed for all compositions whereas a slight decrease for photon energy above 3 eV was observed $(\text{Ge}_1\text{Se}_9)_{85}\text{Cd}_{15}$. k is directly related to the absorption coefficient, α , of the material through the relation:

$$\alpha = \frac{4\pi k}{\lambda} = 2k \frac{2\pi}{\lambda} = 2k \frac{\omega}{C} \quad (6)$$

The increase of the absorption coefficient with the addition of Te or Cd leads to a shift of the absorption edge towards a lower energy. This will also mean a decrease in the energy gap with the addition of Te or Cd [14]. Decrease of the energy gap with Te addition may be attributed to the formation of more Ge-Te bonds, which have lower energies than the Ge-Se bonds, the bond energies of Ge-Se, Ge-Te and Se-Te are 49 kCal $(\text{g atom})^{-1}$, 37.4 kCal $(\text{g atom})^{-1}$ and 40.6 kCal $(\text{g atom})^{-1}$, respectively. Values of the energy gap were determined from plots of $(\alpha h\nu)^{1/2}$ vs $h\nu$ as interception of extrapolation of the linear part with the energy axis, Fig. (4) and Table (1).

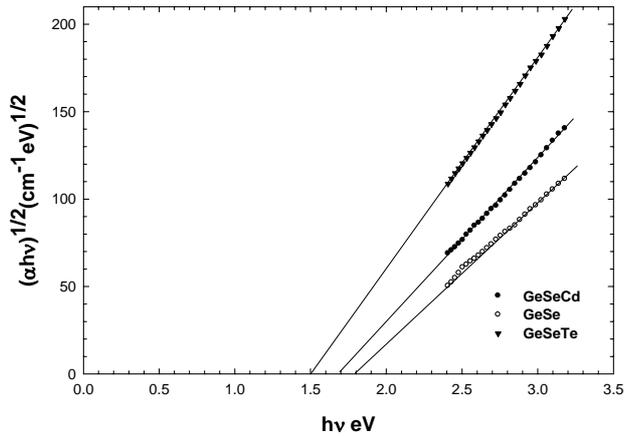


Fig. 4. The variation of the real part of the complex refractive index with the incident photon energy.

The effect of Cd addition on the energy gap was found to be less than that of Te addition. This behavior might also be related to the convolutions of the band edges of each composition and the nature of the electronic transitions involved in the studied range of energy.

Real and imaginary parts of the dielectric function are given by:

$$\varepsilon' = n^2 - k^2, \quad \varepsilon'' = 2nk \quad (7)$$

where C is the speed of light and λ is the wavelength of the incident radiation. Variation of the real (ε') and imaginary (ε'') parts of the complex dielectric function with photon energy is shown in Figs. (5), (6) respectively.

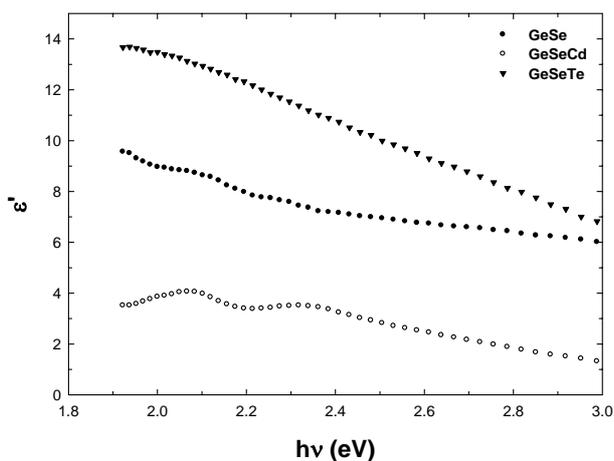


Fig. 5. variation of the real part of complex dielectric function with incident photon energy.

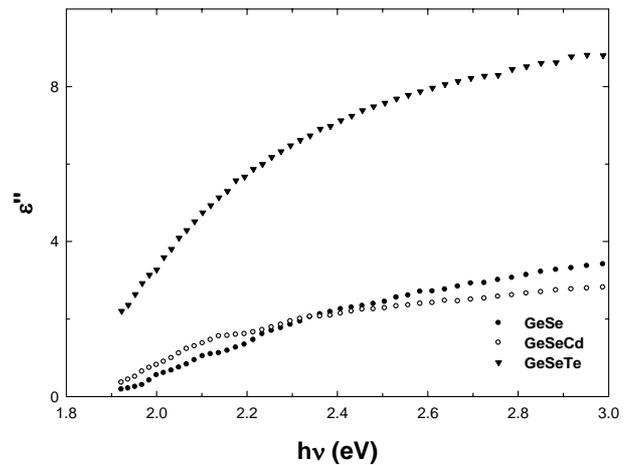


Fig. 6. variation of the imaginary part of complex dielectric function with incident photon energy.

The variation in ε'' for all the studied compositions with photon energy was found to follow almost the same pattern of change. These variations in ε'' are related to the band structure of the relevant compositions. The peaks and valleys appearing in the spectrum are closely related to the convolutions and shape of the band edges in the amorphous semiconductors [15,16]. It was noticed that the addition of Cd leads to lowering in the values of ε'' while the addition of Te will lead to an increase in the values of ε'' . This result could be correlated to the results obtained for the energy gap, as Te causes larger decrease in energy gap than Cd. A further confirmation of the behavior of the optical energy gap with the addition of Cd or Te can also be investigated by plotting $(h\nu \varepsilon''^{1/2})$ against $h\nu$ near the absorption edge. The obtained linear part for each composition is expressed by the relation [17]:

$$h^2\nu^2 \varepsilon'' \approx (h\nu - E_g)^2 \quad (8)$$

where, the obtained linear part indicates that the electronic transition involved is indirect optical transition. Extrapolation of the obtained linear part of each curve will give the value, $E_{g(2)}$, listed in table (1). The obtained results are in close agreement with the results obtained for E_g . The variation of $E_{g(2)}$ was found to follow the same trend as E_g . This pattern of change in optical band gap may be explained on the basis of the change in average bond energy as a function of composition. Since optical energy gap is a bond sensitive property [18], a decrease in the average bond energy results in a decrease in the optical band gap with the addition of Cd or Te to GeSe. At lower concentration of additives (Cd, Te) some added atoms may enter into Se chains resulting in the systematical formation of Se–Cd or Se–Te bonds.

3. Conclusions

The SE technique was used to characterize the effect of two different additives to the amorphous binary composition Ge₁Se₉. The resulting compositions were also found to be amorphous but with higher density than the binary. The average coordination number was found to increase with Te addition and to decrease with Cd addition due to the difference in chemical character of each element. The addition of Cd or Te to Ge₁Se₉ also leads to an increase in the absorption coefficient and a decrease of the energy gap. The addition of Te will lead to an increase of both real and imaginary parts of the dielectric function ϵ' , ϵ'' . Whereas, the addition of Cd leads to a slight increase of ϵ' up to 2.6 eV and then it decreases for higher energies and ϵ'' increases with the addition of Cd. Variations of ϵ'' were discussed in correlation of the energy band structure. These results can lead to the conclusion that one can tailor certain material to have optical constants that are suitable for certain application.

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