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Optical band gap and optical constants of a-$Se_{100-x}Sn_x$ (x= 2, 4, 6 and 8) thin films

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The optical band gap and optical constants of amorphous $Se_{100-x}Sn_x$ (x=2, 4, 6 and 8) thin films, prepared on glass substrates by evaporating in vacuum Se-Sn alloy previously prepared by quenching method, have been studied in the wavelength range 540-900nm. From the measurement of optical transmittance of the films in the mentioned wave length range, the optical band gap (vary from 1.03 to 1.4eV), refractive index (vary from 4.4 to 8), as well as the real and imaginary parts of the dielectric constants were determined. Results indicate that when higher is the Sn-content in the film, lower is the band gap, E_g =1.03eV, and also lower is the refractive index of 4.4 at 900nm. Meanwhile, the real $\varepsilon`_r$ and imaginary part $\varepsilon``_r$ of the dielectric constant were found to decrease with Sn concentration and then increase at 8 at. % of Sn. The observed decrease in the optical band gap is attributed to the corresponding decrease in the average bond energy of a-$Se_{100-x}Sn_x$ films. This result was also confirmed and discussed in terms of the heat of atomization H_s and the average co-ordination number Z.

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Keywords: Optical band gap, Optical constants, Average bond energy, Heat of atomization

1. Introduction

Considerable interest has been devoted over the last two decades to the physical properties of amorphous semiconductors because of their numerous applications. Among amorphous materials, chalcogenide glasses have drawn great attention from scientists and engineers due to their extensive use in solid-state devices. These glasses are used as optoelectronic device material, in integrated optics, optical imaging, optical data storage and infrared optics because of their excellent transmittance, reaching the far- infrared spectral region [1-3]. Since the amorphous films are more transparent than the crystalline ones, therefore the optical properties of semiconducting chalcogenide films have been widely [4-8] investigated and utilized for various applications.

A survey of literature indicates that most of the research work [3,5,9-12] on the optical behaviors of semiconducting chalcogenide films has been carried out on Te-based material. The selection of Te-based alloys in these studies arises from their applicability as recording materials and because the thermal conductivity of Te-based films is small so that recording is sensitive to laser energy. However, the drawback of Te-based materials is their poor resistance to oxidation [5] and degradation in moist atmosphere [13]. To overcome these problems several attempts [14-17] have been made to investigate Se and Se-based films as they have applications in device technology. Although pure amorphous selenium films exhibit optical absorption and photosensitivity in the visible range of wavelength, but Se-based films exhibit the same properties over a larger wavelength range [18]. Among Se-based films, metal chalcogenides offer a range of optical band gaps suitable for variety of optical and optoelectronic applications [19,20]. Tin selenide may be used in memory switching devices, in holographic recording systems and as an efficient solar material [21]. Although optical band gaps of single crystals and polycrystals thin films of SeSn have been investigated by workers [20, 22-24] but less attention has been paid to amorphous SeSn thin films. The purpose of the present paper is therefore to report the measurements of the optical band gap and optical constants of a-$Se_{100-x}Sn_x$ (x= 2, 4, 6 and 8) films. In this regard the optical band gap has been deduced for all films and its correlation with average bond energy, heat of atomization and co-ordination number has been studied. Besides to that, the refractive index and the extinction coefficient were also evaluated and used for the calculation of the real and imaginary parts of the dielectric constant.

2. Experimental

Glassy alloys of $Se_{100-x}Sn_x$ (x=2, 4, 6 and 8) were prepared by a quenching method. High purity (99.999%) of Selenium and Tin in appropriate atomic percent proportions was weighed in a quartz glass ampoule (length 5cm and internal diameter 8 mm). The content of the ampoule was sealed in a vacuum of about 10^{-5} torr using an oxygen LPG torch. The sealed ampoules were kept inside a programmable furnace where temperature was raised at a rate of 3-4^oC per minute up to 900^oC and kept around that temperature for 10h. The ampoules were frequently rocked to ensure the homogeneity of the sample. The ampoules having the material in molten state were then rapidly quenched in ice cooled water. The ingots

of the sample were then taken out by breaking the ampoules. The ingots of the samples were grinded into fine powder and their amorphous nature was confirmed by XRD.

Thin films of glassy alloys of a-$Se_{100-x}Sn_x$ of thickness 2000Å were deposited on a glass substrate by vacuum evaporation technique, keeping the substrate at room temperature and in a vacuum of 10^{-5} torr using a molybdenum boat. The films were kept inside the vacuum for 24h to attain metastable equilibrium, as suggested by Abkowitz [25]. Film's thickness was measured using a single crystal thickness monitor and the elemental composition was ascertaining through the use of EDX. The absorption, reflection and transmission of the thin films were measured using Hitachi-330 double beam spectrophotometer. The measurements were carried, out at room temperature, with wavelength in the range 540-900 nm in steps of 20 nm.

3. Results and discussion

Determination of the optical constants, e.g. refractive index *n* and extinction coefficient *k*, of a material is possible from its optical behavior i.e. from the reflectance and transmittance data obtained from the spectrophotometric measurements. Thin films are ideal specimens for reflectance and transmittance type of measurements. The theory of reflectance of light from thin films is expressed in terms of Fresnel's coefficients. That is considering air as one medium n_o=1, and the film as a second medium which is highly absorbing in nature, the reflection relation may be [14-17, 26-29] written as,

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

where *k* is the extinction coefficient and *n* is the refractive index. The absorption coefficient α is given by,

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

The absorption coefficient α can be obtained from the absorbance, given by the ration I_o/I_d, where I_o is the incident intensity and I_d is the intensity after traversing a thickness d in the film. It is suggested that [14-17, 26-29] the absorption coefficient optical density *OD*/ thickness *d*, or

$$\alpha = \frac{OD}{d}$$
$$\alpha = \left(\frac{1}{d}\right)\log\left(\frac{I_o}{I_d}\right) \quad (3)$$

Using the above three equations the optical constants were calculated.

It is well known that in crystalline materials, the electronic transition occurs at absorption edge corresponding to the minimum energy difference between the lowest energy of the conduction band and the highest energy of the valence band, while in amorphous materials a different type of optical absorption edge is observed. It is reported [30] that in chalcogenide glasses the absorption coefficient increases exponentially with the photon energy (*hν*) near the energy gap. This optical absorption edge is known as the Urbach edge [31, 32] and is given by

$$\alpha = \alpha_o \exp(h\nu / E_e) \quad (4)$$

where α_o is a constant and E_e is the width of the band tail of the localized states in the band gap. Fig. 1 shows the variation of the absorption coefficient *(α)* against the incident photon energy *(hν)* for a-$Se_{100-x}Sn_x$ (x =2, 4, 6 and 8) thin films. It is clear that the absorption coefficient increases with increasing photon energy for all films of a-SeSn in the composition range of investigation. Furthermore, Fig. 1 demonstrates that the exponential behavior of the absorption edge as determined by Eq.(4) is satisfied in glassy films under study and the calculated values of *(α)* are of the order of 10^4 cm^{-1} which agree fairly well with the results obtained by other workers [15,17,33]. However, at higher values of absorption coefficient, it is suggested [34] that the absorption takes the following form,

$$\alpha = \frac{A(h\nu - E_g)^r}{h\nu} \quad (5)$$

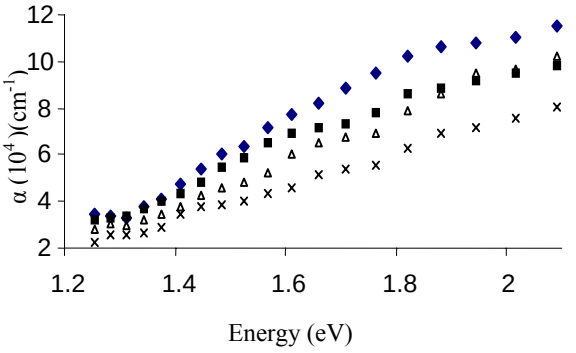

Fig. 1. Absorption coefficient (α) against photon energy in a-$Se_{100-x}Sn_x$ thin films: (◆) x=2, (■) x=4, (▲) x=6, (x) x =8.

Where *A* is a constant, E_g is the optical band gap of the material and *r* is an index, which characterized the transition process. For allowed direct and indirect transition *r* has the values of ½ and 2 [17], respectively. To obtain the optical band gap of the films, it is required to plot $(\alpha h\nu)^{1/r}$ against *(hν)* for the said values of *r* and determine the value of *r* that fit Eq.(5). It is found that the value of *r* which most fit Eq.(5) comes out to be 2. Fig. 2. Shows the dependence of $(\alpha h\nu)^{1/2}$ on the photon energy *(hν)* for a-$Se_{100-x}Sn_x$ of different compositions, which indicates that allowed indirect transition is responsible for transition in a-$Se_{100-x}Sn_x$ thin films. To determine the optical band gap, E_g of the films, the linear portion of the plot is extrapolated to intersect the photon energy axis. The obtained values of E_g are listed in Table 1 and indicate that the optical band gap decreases with increasing Sn

concentration in the films. This may be understood on the basis of the change in the average bond energy of the a-SeSn film as a function of composition. It is suggested [35] that the single covalent bond energy of heteronuclear bonds *D(A-B)* can be calculated using the single covalent bond energy of homonuclear bonds *D(A-A)* and *D(B-B)* and the electronegativity, X_A of atom *A* and X_B of atom *B* through the formula,

$$D(A\text{-}B) = [D(A\text{-}A)\ D(B\text{-}B)]^{1/2} + 30(X_A - X_B)^2 \qquad (6)$$

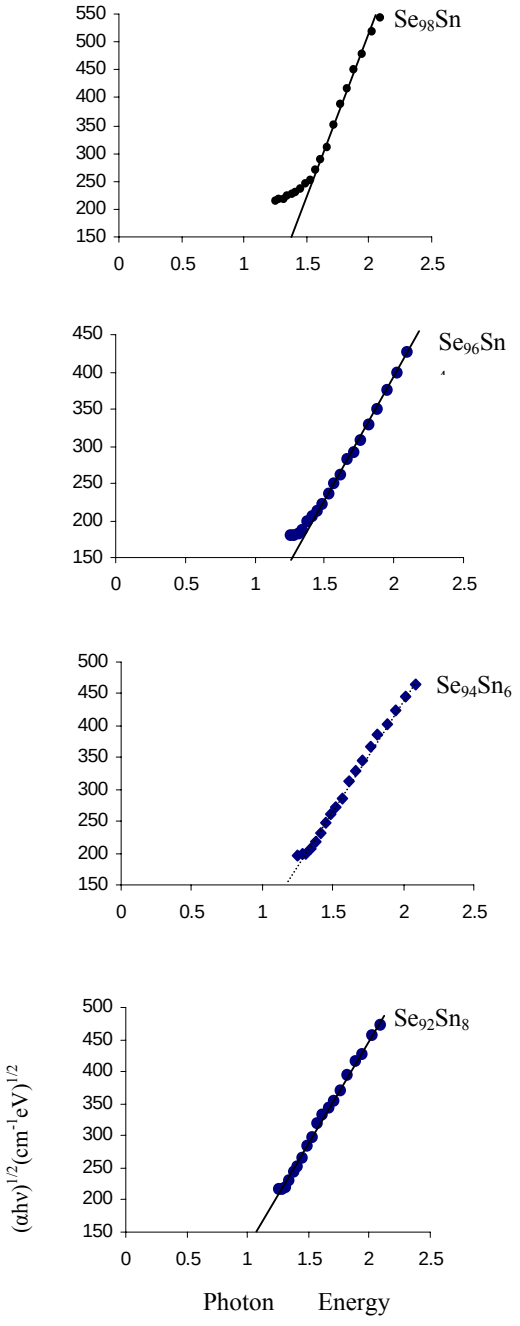

Fig. 2. Plot of $(\alpha h\nu)^{1/2}$ against photon energy (hν) in a-$Se_{100-x}Sn_x$ thin films.

Table 1. Energy band gap E_g, heat of atomization H_s, Co-ordination number Z, and average single-bond energy H_s/Z.

Alloy	E_g(e.V)	H_s(kJ/mole)	Co-ordination Number Z	Average single-bond energy H_s/Z
$Se_{98}Sn_2$	1.40	208.3	2.04	102.10
$Se_{96}Sn_4$	1.25	210.2	2.08	101.10
$Se_{94}Sn_6$	1.16	212.3	2.12	100.16
$Se_{92}Sn_8$	1.03	214.1	2.16	99.12

The single bond energy values of Se-Se and Sn-Sn as given in literature [36] are 332.3 kJ/mol and 195.2kJ/mol, respectively. The electronegativity values for different elements, obtained by Husain et al [37] using equalization principle of Sanderson [38], were used for estimating bond energy of Se-Sn and come out to be 265.1 kJ/mol. When Sn is added some kind of atomic rearrangement takes place and hence Se-Sn bonds replace some of Se-Se bonds, as a result of which the average bond energy of $Se_{100-x}Sn_x$ films decreases. Since the optical band gap is a bond sensitive property, therefore a decrease in the average bond energy is responsible for the corresponding decrease in the optical band gap. This has been confirmed through the calculation of the heat of atomization H_s *(A-B)* of a binary semiconductor [30] and the average co-ordination number *Z* using equations (7) and (8):

$$H_s(A\text{-}B) = \Delta H + [H^A{}_s + H^B{}_s]/2 \qquad (7)$$

where ΔH is the heat of formation and is proportional to the square of the difference between the electronegativities of the two atoms *A* and *B*. However, since ΔH is equal to 10% of the heat of atomization [17] it may be neglected. $H^A{}_s$ and $H^B{}_s$ are the heat of atomization of atoms *A* and *B*, respectively. The heat of atomization of Se(206.5kJ/mol) and that of Sn (301.8 kJ/mol) were taken from literature [36]. The obtained values of H_s(Se-Sn) ,as calculated from Eq.(7), are given in Table 1.

The average co-ordination number [39] of a binary semiconductor $Se_{100-x}Sn_x$ is calculated using Eq.(8):

$$Z = xN_{Sn} + (1\text{-}x)N_{Se} \qquad (8)$$

where N_{Sn} and N_{Se} are the co-ordination numbers of Sn, equal to 4, and Se, equal to 2, respectively. The values of *Z* for the samples under studies are given in Table 1. The average single-bond energy (H_s/Z) in the alloy has also been calculated and given in the same table. It is clear that E_g as well as H_s/Z decrease with increasing Sn contents and is in consistent with our results regarding the linear relationship between the band gap and the bond energy. The same behavior has also been observed in Se-Sb [17] and S-As [40] chalcogenide glasses.

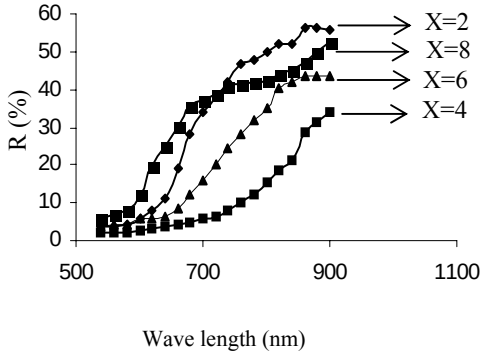

Fig. 3. Variation in reflection with wave length in a-$Se_{100-x}Sn_x$ thin films.

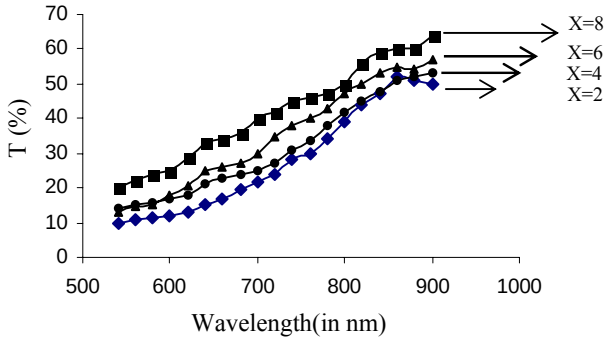

Fig. 4. Variation in transmission with wavelength in a-$Se_{100-x}Sn_x$ thin films.

Figs. 3 and 4 depict, respectively, the variation of reflectance *R* and transmittance *T* with wavelength for a-$Se_{100-x}Sn_x$ alloys. From these figures it is evident that both the reflectance and transmittance increase with the increase in wavelength. The spectral dependence of *n* and *k*, as calculated from Equs. (1) and (2), are shown in Figs. 5 and 6, respectively. It has been observed that *n* decrease, while the extinction coefficient *k* increases with photon energy. Furthermore, it was noticed that at particular photon energy both *n* and *k* decrease with increasing Sn concentration in the a-$Se_{100-x}Sn_x$ system. A similar trend has also been reported [5, 30] for other amorphous semiconducting thin films.

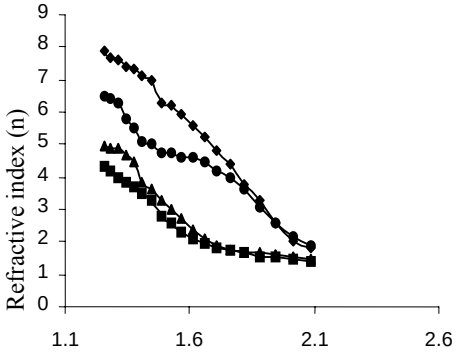

Fig. 5. Variation in refractive index (n) with photon energy in a-$Se_{100-x}Sn_x$ thin films: (♦)x= 2, (●) x=4 ,(▲) ,x=6 ,(■)x=8.

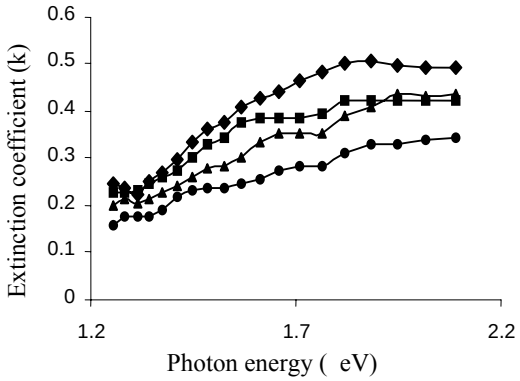

Fig. 6. Extinction coefficient (k) against photon energy in a-$Se_{100-x}Sn_x$ thin films: (◆) x=2, (■) x=4, (▲) x= 6, (●) x=8.

The real $\varepsilon`_r$ and imaginary $\varepsilon``_r$ parts of the dielectric constant for a-$Se_{100-x}Sn_x$ films was also calculated using the relation [41],

$$\varepsilon`_r = n^2 - k^2 \qquad \text{and} \qquad \varepsilon``_r = 2nk \qquad (9)$$

Figs. 7 and 8 show the variation of these two parameters with photon energy. From these two figures it is clear that both $\varepsilon`_r$ and $\varepsilon``_r$ decrease with Sn concentrations, attain their lower value at 4 at. % of Sn, and then increase at 6 and 8 at.% of Sn. It is reported [5] that the decrease in $\varepsilon``_r$ is related to the energy loss of the charge carriers. Accordingly, it is reasonable to state that at 2 at.% of Sn the charge carriers absorbed more energy giving rise to the large absorption coefficient. With further increase of Sn the amount of energy absorbed by the sample decreases and is reflected on the corresponding values of *R* as it is seen from Fig. 1.

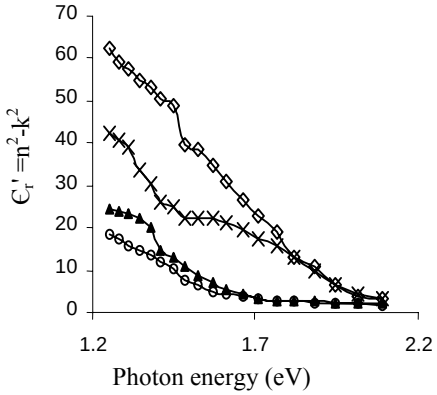

Fig. 7. Real part ($\varepsilon_r' = n^2-k^2$) of the dielectric constant against photon energy in $Se_{100-x}Sn_x$ thin films: (◇) x=2, (○) x= 4, (▲) x=6, (x) x= 8.

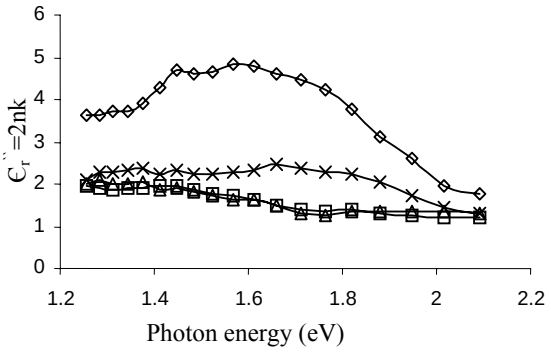

Fig. 8. Imaginary part (ε``= 2nk) of the dielectric constant against photon energy in a-$Se_{100-x}Sn_x$ thin films: (◇) x=2, (□) x=4, (△) x=6, (x) x=8.

4. Conclusion

Based on the present optical investigation of a-$Se_{100-x}Sn_x$ films the following conclusions can be drawn:

The films under consideration were found to have a large absorption coefficient (~ 10^4 cm^{-1}) and, therefore, they may have an industrial application as a medium for optical disk because of their large absorption coefficient.

The enhancement of the density of defect states, monitored by the reduction of the optical band gap, facilitates the transition of the carriers between the localized states.

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