Effect of Composition and Annealing on Some of the Optical Parameters of $Ge_x Te_{100-x}$ Thin Films

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The dependence of the absorption coefficient α on photon energy hv was determined in the spectral range from 1.1 to 3.9 eV at room temperature, for evaporated $Ge_x Te_{100-x}$ films. The variation of the optical gap E_g^{opt} , dielectric constant ε , and absorption coefficient, α with composition and annealing are reported. The optical gap increases with x followed by a sharpe decrease beyond x =20. This can be explained in terms of increase in the number of Te-Te bonds and formation of $GeTe_4$ tetrahedral with an increase in the chalcogen content. The observed behaviour is explained on the basis of chemical bond approach and on Mott and Davis model for the density of states in amorphous solids. The absorption coefficient for Ge -Te films exhibits exponential dependence on photon energy obeying Urbach's rule in the absorption edge . The optical absorption measurements on the as-deposited and annealed films indicate that the absorption mechanism is due to direct transition. The optical gap E_g as well as the high frequency dielectric constant, ε , depends on the film composition and the annealing temperature. The shift in the absorption edge due to the heat treatment is explained by a change in the defect structure of the films. The decrease in the optical gap after annealing is due to the effect of oxidation . The optical gap, E_g^{opt} , as well as the high frequency dielectric constant , ε , depends on the annealing temperature.

Introduction

The existence of a critical composition at X = 20 for the $A_X^{iv} B^{vi}_{100-x}$ system of glasses has been discussed earlier on the basis of Phillips constraints theory [1]. According to this theory, the composition at X = 20 in these systems gives rise to an ideal glass in which the number of operative constraints is equal to the number of degrees of freedom. Silicon and germanium form good glasses with chalcogen elements over a wide range of compositions and those glasses exhibit some interesting physical properties. Amorphous $Ge_x Te_{100-x}$ alloys are of interest, partly because their structural transformation is associated with memory switching properties , and partly because their local atomic arrangement are quiet different from those of crystalline GeTe [2].

Chalcogenide glsses have extensive applicatrions as electronic and optoelectronic   device material [3]. This class of materials containing a large percentage of chalcogen element is widely used in switching and memory devices [4,5]. An understanding of the dependence of various properties of such chalcogenide glasses on composition is important, because the continuously variable composition of these alloys may be utilised to prepare materials for particular applications.

The optical properties of amorphous semiconductors have been the subject of many recent papers [6,7]. It is well known that the optical gap of amorphous semiconductors alloys strongly depends on their compositions [6,7]. The study of the optical constants of materials is interesting for many reasons. First, the use of materials in optical fibers and reflected coating requires accurate knowledge of their optical constants over wide ranges of wavelength .Second, the optical properties of all materials are related to their atomic structure, electronic band structure and electrical properties .

The structural bonding between the neighbours determines the optical properties, such as absorption and transmission of the amorphous material . The general features of the density of states of amorphous solids can be obtained from the model proposed by Mott and Davis [8].

This work deals with the optical processes that occur for photons having energies comparable to that of the band gap. For most semiconductors , this means photons in the visible regions of the spectrum since gaps often lie in the range from 1 to 3 ev. The annealing may provide a deeper insight into the mechanism of disorder and defect formation in the amorphous chaccogenide. this paper aims to study the effect of compositions and annealing on some of the optical parameters of the $Ge_x Te_{100-x}$ alloys by means of the spectral dependence of the absorpance A, transmittence T, and reflectance R, in the spectral range from 200 to1100 nm.

Experimental

High purity (99.999 %) Ge and Te (Aldrich)in appropriate proportions were weighted into a quartiz glass ampoule (12mm diameter) the contents of the ampoule (15 g total) were sealed at a prssure of 10^{-4} torr and heated in a rotating furnace at around 1300 K for 24 h the melt was quenched in water at 273K to obtain the glass.

Amorphous Ge_x Te E_{100-x} films $(12.5 \leq X \leq 22.5)$were prepared by evaporation under vacuum of 10^{-6} torr using an Edward coating unit E 306 .Films were deposited on ultrasonically cleaned glass slide. The film thickness was accurately determined using a quartize crystal monitor, Edwards model FMT5 .The rate of the film deposition was measured using the same FMT5 quartze crystal monitor. The freshly prepared films were examined. The optical absorption and transmission data were obtained using a computerized SHIMADZU UV-2100 double beam spectro-photometer. The measurements were carried out in wavelenghts in the range 200 to 1100 nm with 10 nm steps. The samples were thermally annealed at different temperatures . All the optical measurements were carried out at room temperature.

Results
Optical energy gap:

As explained by Tauc [9], there are three different regions in the optical absorption curve for an amorphouse semiconductor corrosponding to three different ranges of absorption coefficients. In the first region the absorption coefficients, $\alpha < 1$ cm^{-1}, the second region corrosponds to an absorption in the range $1<\alpha<10^4$ cm^{-1}. A high value for the absorption coefficient $(\alpha >10^4$ cm$^{-1})$ marks the third region [9].

The fundamental absorption edge in e most amorphous semisconductors follows the exponential law. Above the exponential tails, the absorption of amorphous semiconductor has been observed to obey the equation [9]:

$$\alpha h\nu = B (h\nu - E_g^{opt})^r \qquad (1)$$

Where $\alpha h\nu$ is the absorption coefficient of an angular frequency of $\omega = 2\pi\nu$, B is a constant and r is an index which can be assumed to have values of 1/2, 3/2, 2 and 3, depending on the nature of the electronic transition responsible for the absorption. r =1/2 for allowed direct transition , r = 3/2 for forbidden direct transition and r =3 for forbidden indirect transition[10]. The range in which this

equation is valid is very small and hence it become too difficult to determine the exact value of the exponent (r), [11].

The value of the optical gap E_g^{opt}, in the amorphous materials is obtained by plotting $(\alpha h\nu)^{1/r}$ in the high absorption range followed by extrapolating the linear region of the plot of $(\alpha h\nu)^{1/r} = 0$. This extrapolated value is used to define the so called optical gap in amorphous materials. The relation between $(\alpha h\nu)^{1/r}$ and $h\nu$ (r = 1/2, 3/2, 2, and 3), for as-deposited $Ge_{.12.5}Te_{.87.5}$ thin films, is shown in Fig. 1. From this figure it is shown that the value of r =1/2 should be a linear relation most fit for equation 1. This indicates that allowed direct transitions are responsible for absorption for all compositions of GeTe films .

The first analysis of the absorption curves was made on the assumption that absorption results from direct or indirect transition between parabolic bands for which the following relations hold respectively [12].

For direct transition, the absorption coefficient, α, is given by the following relations obtained by Mott and Davis [6]:
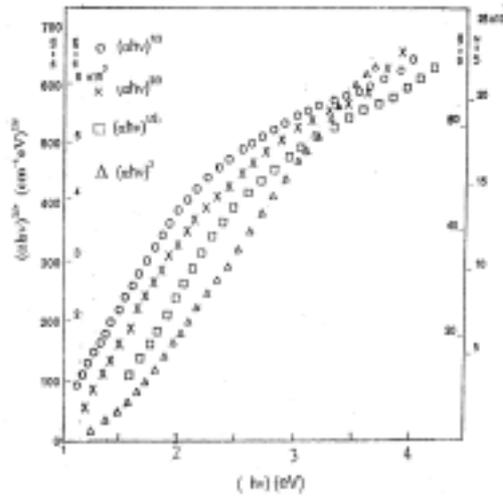

Fig.(1) $(\alpha h\nu)^{1/r}$ vs. hν plots for as-deposited $Ge_{12.5}Te_{87.5}$ Films.
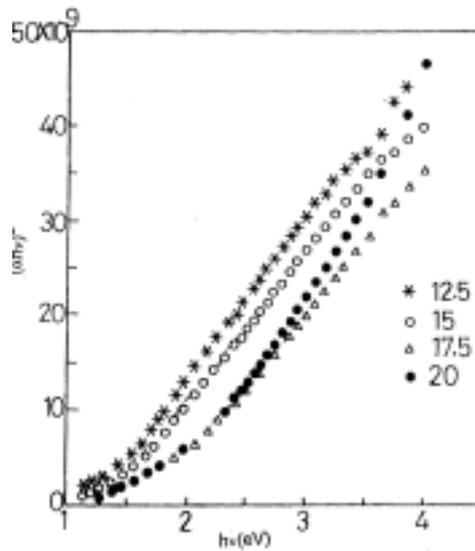

Fig.(2) $(\alpha h\nu)^2$ and hν plots for as-deposited $Ge_x Te_{1-x}$ Films With x = 12.5,15 ,17.5 and 20 at.%.

$$(\alpha h\nu)^2 = B ((\alpha h\nu - E_g^{0pt}) \qquad (2)$$

and for indirect transition

$$(\alpha h\nu)^{1/2} = A (\alpha h\nu - E^{0pt}_g) \qquad (3)$$

where A and B are constants and E^{opt}_g is the optical gap. The usual method for determination E^{opt}_g involves plotting a graph of $(\alpha h\nu)^2$ for direct and $(h\nu)^{1/2}$ for indirect transition versus photand ħω for Geat.%) thin films .Fig. 3 shows the relation between $(\alpha h\nu)^2$ and hν for $Ge_{0.2}$ $Te_{0.8}$ thin films at different annealing temperature. These two figures (2,3) show the linear relation obtained for higher values of absorption satisfy eqn.2. The nature of the absorption curves is found to be identical to that of the elemental amorphous semicondu- ctors [13, 14]. The calculated values of E^{opt}_g for direct transition and constant B are given in Table1.
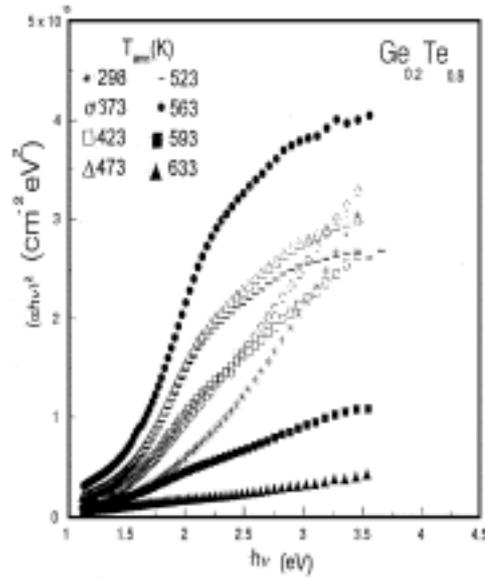

Fig.(3) $(\alpha h\nu)^{1/r}$ vs. hν plots for $Ge_{0.2}$ $Te_{0.8}$ Films annealed at different temperatures .
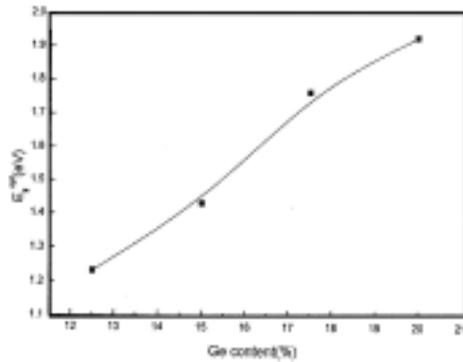

Fig.(4) The relation between Ge content and E_g^{opt} For as-deposited Ge_xTe_{1-x} Films .
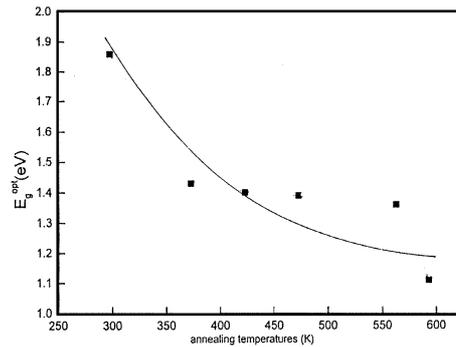

Fig.(5) The relation between annealing temperatures and E_g^{opt} For annealed $Ge_{0.2}Te_{0.8}$ Films .

Table 1

X at%	E_g^{opt} (ev)	$B * 10^6$ (cm^{-1} Ev^{-2})	(N /m *) 10^{21} (cm^{-3})	ε_∞
12. 5	1.233	1.95	9.58	22.86
15	1.432	1.73	8.92	18.32
17.5	1.765	1.78	7.6	12.89
20	1.933	2.04	8.26	14.26

It is found that the optical gap increases with increasing the germanium contents, as shown in Fig.4. The calculated values of E_g^{opt} for direct transition at different annealing temperature are given in Table 2.

Table 2

Annealing Temperature (K)	E_g^{opt} (eV)	(N/ m*) $\times 10^{21}$ (cm^{-3})	ε_∞
298	1.86	15.01	21.50
373	1.43	16.13	26.25
423	1.40	13.44	24.43
473	1.39	10.59	25.96
563	1.36	9.28	31.31
593	1.11	1.95	410.51

It is shown that the optical gap decreases with increasing the annealing temperature, as shown in Fig.5.

High frequency dielectric constant:

It is known, that if multiple reflection are neglected, the transmittance, T , of a perfectly smooth substrate is determined by the the following relation [15, 16] :

$$T = (1 - R)^2 \exp(-A) = (1 - R) \exp(-\alpha d) \qquad (4)$$

where R is the reflectance, A is the absorptance, α in cm^{-1} is the optical absorption coefficient and d is the film thickness.

For a better understanding of the physical properties of this material, it is interesting to study some optical constants used to describe the optical properties, e.g. the high frequency dielectric constant , $\varepsilon`$, which is related with the square of wavelength, λ^2 , by the following equation [17] :

$$\varepsilon` = n^2 = \left(\frac{1+\sqrt{R}}{1-\sqrt{R}}\right)^2 = \varepsilon_\infty - \frac{e^2 N}{\pi c^2 m^*} \lambda^2 \qquad (5)$$

where n is the refractive index , e is the electronic charge and c is the velocity of light. From this equation, the high frequency component of the relative permittivity, ε_∞, and the ratio of the carrier concentration N to the effective mass, m*, (N/m*) could be determined. Fig.6 shows the relation between the relative permitivity, ε' and λ, for the as-deposited Ge$_x$ Te$_{1-x}$ films .It could be

noticed that the relative permitivity decreases exponentially with increasing λ^2. To obtain the high frequency dielectric constant eq. 5 was applied on the linear parts of these curves. The values of ε_∞ and (N/m*) are given in Table 1 .
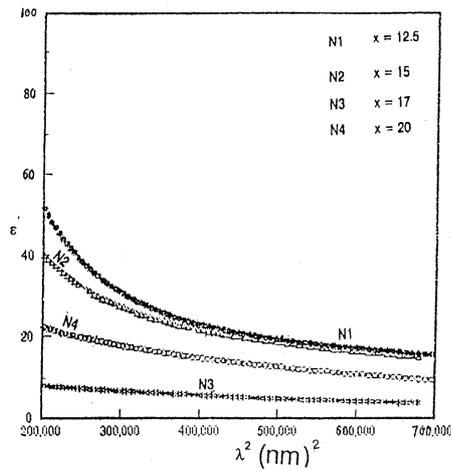

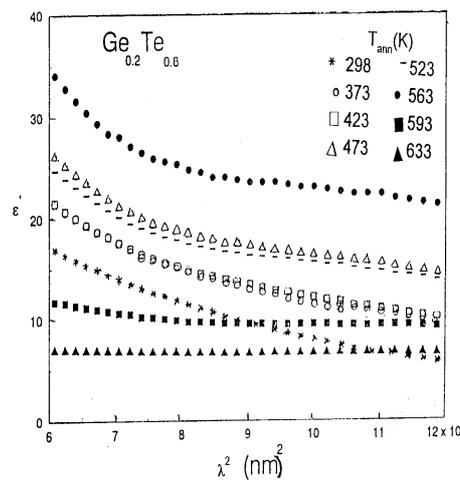| **Fig.(6)** The relation between ε' vs. λ^2. for as-deposited $Ge_x Te_{1-x}$ Films With x = 12.5,15 ,17.5 and 20 at.%. | **Fig.(7)** Relative permitivity ε' and λ^2 $Ge_{0.2}$ $Te_{0.8}$ Films annealed at different temperatures. |

Fig. 7. Shows the relation between relative permitivity ε' , and , λ^2 for $Ge_{0.2}Te_{0.8}$ films annealed at different temperatures . The values of ε_∞ and (N/m*) are given in Table 2 .

Discussion

The results have been interpreted in terms of current theories. Mott and Davis theories and atomic structure of Ge_xTe_{1-x} . The general features of the density of states of amorphous solids can be understood from the model proposed by Mott and Davis [6, 8]. The increase of the optical gap with increasing Ge content up to x < 20 can be attributed to decrease of the width of localized states near the mobility edges, so the disorder and defect present in the structure decrease.In particular, it is known that unsaturated bonds together with some saturated bonds (like dative bonds are produced as a result of an insufficient number of atoms deposited in the amorphous films[18].

The unsaturated bonds are responsible for the formation of some defects in the films. Such defects produced localized states in the amorphous solids. The presence of a high concentration of localized states in the band structure is responsible for the low values of E_g^{opt}. The increase of the optical gap for low concentration of Ge atoms (x<20at.%) may be due to stastically

uniform distribution of Ge Te$_{4/2}$ structural units in the Te rich glass. According to Phillips constraint theory[1], the glass with x = 20 at.%, is ideal glass in which the number of operative constraints is equal to the number of degree of freedom, the stable tetrahedral units are formed .For higher concentration of Ge (x >20 at.%) the number of the homopolar bonds increases with increasing quantitative disorder and introduce extra localized states between the mobility edgs .Optical absorption from these states could then shift the absorption edge and decrease the opticl gap.

The behaviour of the optical gap shown by Ge -Te glasses in the range of compisitions studied here, can be explained on the bases of chemical bonding and change in the short-range order. The chemically ordered network (CON) structure, is more suitable for explaining the behaviour exhibited Ge-Te glass than the continuous randum network (CRN) model. According to the (CON) model for Ge$_X$Te$_{1-X}$ glass system, three possible types of bonds, Ge - Te, Te - Te and Ge-Ge exist. The variation of the optical energy gap with compositions can be explained on the bases of the distribution of different types of these bonds.

The observed exponential tail of the absorption edge (Fig. 2) is similar to those observed in amorphous Se and Ge [19]. Dlanyon [20] has explained the exponential tail in amorphous Se films as due to the exponential distribution of the density of states in the tail region of the valence band .A similar explaination in terms of an exponential tail of the valence band may beaffered for our observations on amorphous Ge Te films. Anderson [21] and Mott [22] suggested that, localization may occure up to higher levels in the valence band than in the conduction band due to the predominance of vacancy like defects in the amorphous material. The localized levels which form continous, act as trapping states.

It could be noticed that the dielectric constant ,ε and the ratio N/m* decrease with increasing the Te content and annealing temperature. It could be interpreted that for covalently bonded system, the major contribution to susceptibilities come from electronic transitions between bonding and antibonding states. In general it can be concluded that ε and N/m* are related to the internal microstructure as can be emphasized by considering the results in Tables (1,2) together with those in Figs.(6,7) most of the change in the N/m* ratio is regarded as a corresponding change in N [23].

It is reasonable to suppose that the thin films contain an increased number of homonuclear bonds in comparison with the chemically ordered bulk samples which were prepared from the melt. Thin film growth takes place at temperature below the melting point of the material. Thus the ordering processes are hindered.Annealing causes a breaking of homonuclear bonds and

a formation of energetically more favored heteronuclear bonds. In this way the random network is partially changed approaching a more chemically ordered structure.

The optical gap decreases from 1.86 eV to1.11 eV with increasing the annealing temperature from 298 K to 593 K (Fig .5) , and the optical absorption edge shifts , when evaporated films are annealed .It is known that unsaturated bonds together with some saturated bonds (like dative bonds) are produced as a result of an insufficient number of atoms deposited in the amorphous films [18]. The unsaturated bonds are responsible for the formation of some defects in the film. Such defects produce localized states in the amorphous solids.The presence of high concentration of localized states in the band structure reducing the optical gap. The transition probabilityof the carriers is higher across the smaller optical gaps between localized states of evaporated amorphous films. The larger absorption coefficient due to higher transition probability of carriers across the smaller optical gap may be explain the variation of the absorption coefficient and decreasing the optical gap.

The decrease in the optical gap with annealing for $Ge_{0.2}Te_{0.8}$films can be interpreted as the annealing of germanium chalcogenide films decreases the homopolar bond density by an order of magnitude.The defictive bond can be activated by photons having the same band gap energy and subsequently oxideze [24]. In these processes, the dangling bonds and Ge-Ge homopolar bonds transformed to Ge-O bonds [24], which creat defect in $Ge_{0.2}Te_{0.8}$ films. On the other hand, the decrease in the optical gap of the amorphous film can be caused by the increased tailing of the conduction band edge into the gap due to enviroment contamination during heat treatment [25].

Conclusion

The experimental results indicated that the absorption coefficient for Ge_xTe_{1-x} films exhibits an exponential dependence on photon energy, obying Urbach rule in the absorption edge for this film. The optical gap is strongly dependence on the film compisition. The absorption mechanism for Te_xSe_{1-x} films is due to direct transitional higher incident energies. For high concentration of Te values of E^{opt}_g, ε_∞ and N/m^* are sensitive to the Te content.

The optical gap decreases with increasing the annealing temperature. This behaviour is explained as the unsaturated bonds are responsible for the formation of some defects which produce localized states in the films. Such defects produce localized states in the band structure reducing the optical gap.

References

1. J . C . Phillips, J . Non-Cryst Solids, 43, 37 (1981).
2. T . Okabe and M . Nakagawa, J . Non-Cryst Solids, 88, 182 (1986) .
3. D . Adler , Sci . Amer . , 236, 36 (1977).
4. S . R . Ovshinsky , Phys . Rev . Lett . , 21, 1450 (1968).
5. R . Zallen , " The Physics of Amorphous Solids " , (Willey, New York , 1983)
6. N . F . Mott and E . A .Davis , " Electronic Process in Non-Crystalline Materials ", (Clarendon Press , Oxford , 1979).
7. E . A . Davis , "Electronic and Structural Properties of Amorphous Semiconductors" , Eds . , P . G . Lecomber and J. Mort , Academic , London and New York p.425 (1973).
8. N . F . Mott and E . A .Davis , " Electronic Process in Non-Crystalline Materials " , (Clarendon Press , Oxford , 1971).
9. J. Tauc . , " Amorphous and Liquid Semiconductors " , Ed . J .Tauc , (Plenum Press New York 1974) .
10. R . A . Smith , Phil. Mag. Suppl. , 2, 81 (1953).
11. M . Cohen , H . Frizsche and S . R . Ovshinsky , Phys. Rev . Lett . 22, 1065 (1969).
12 . J . Tauc , R . Grigorovichi and A . Vancu , Phs. Stat. Sol . , 15 627 (1966).
13. S . Chaudhuri , S . K . Biswas , A . Choudhury and K . Goswami , J . Non - Cryst . Solids , 54, 179 (1983).
14. M . D . Guilo , D . Manno , R . Rella , P . Siciliano and A . Tepore , Solar Energy Mater. , 15, 209(1987).
15. M . Becker and H . Y . Fan , Phys . Rev. , 76, 1530 (1949).
16. T . S . Moss , " Optical Properties of Semiconductors " , (Butter) Worths , London , 1959.
17. W.G.Spitzer and H.Y.Fan , Phys.Rev. 106, 882 (1957).
18. M . L . Theye , (Proc. Fifth Int . Conf . on Amorphous and Liquid Semiconductors) , Vol . 1 , Garmisch , Germany , (1973) Taylor and Francis , London , 1974).
19. A . H . Clark , Phys. Rev. , 154, 750 (1967).
20. H . P . Dlanyon , Phys . Rev. , 130, 134 (1963).
21. P . W . Anderson , Phys . Rev . , 109, 1458 (1958).
22. N . F . Mott , Phil . Mag. , 19, 835 (1969) .
23. N . S . Lidorenko , O . B . Sokolov , A . S . Kagan , I . M. Rombe and A . A . Vagin , Sov . Phys. Dokl . , 16, 133 (1971).
24. R . J . Nemanich , G . A . N . Comnell and T . M. Hayes , Phys . Rev. , B 18, 6900 (1978).
25. R . A .Street , Solid State Comm . , 42 , 363 (1977).