The composition dependence of the optical band gap in Ge–Se–In thin films

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Abstract

Bulk glasses with the chemical composition $Ge_y Se_{94-y} In_6$ ($8 \leqslant y \leqslant 30$ at%) have been prepared from high purity constituent elements. Fragments of the bulk glasses are used to deposit thin films by vacuum thermal evaporation. The optical band gaps (E_g s) of the as-deposited films have been measured. The allowed optical transition is found to be indirect. The relation of E_g to the covalent coordination number, Z, is demonstrated by varying the composition parameter y of the thin films. A maximum in the compositional dependence of E_g is attained at $Z = 2.63$. The cohesive energies (CE) of the investigated samples have also been calculated using the method suggested by the chemical bond approach. It is found that the composition dependence of the CE also possesses a peak at $Z = 2.63$.

A plausible explanation based on the bonding considerations between the constituents has been provided for the understanding of the E_g-Z and CE-Z dependences for these Ge–Se–In thin films.

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1. Introduction

Amorphous multicomponent chalcogenides have recently gained considerable attention due to their interesting optical properties and technological applications. Their promising material science applications include photostructural optical recording [1,2], advanced IR optical fiber [3], and acousto-optic devices [4,5]. They are often preferred to their crystalline counterparts with similar properties because of their favorable mechanical and interfacing properties. Additionally, the absence of long-range order allows the modification of their optical properties to a spe-

cific technological application by continuously changing their chemical composition. Hence, the study of the dependence on composition of their optical properties is of great importance to improve the understanding of the mechanisms underlying these phenomena and also to improve their applications in technology.

The Ge–Se–In ternary is a prototypical chalcogenide system and forms bulk glasses over a large range of compositions extending to about 15 at% In and about 60–90 at% Se, with the remainder being Ge [6]. Thus, it is possible to scan with one glassy family a very wide range of covalent coordination number, Z. This system is, therefore, ideal for the analysis of the variation of a given physical property with Z. However, the calculation of the key parameter, Z, requires the knowledge of the coordination numbers (CN) of all the constituents of the alloy. For the system under investigation, the CN(Ge) and CN(Se) respect the

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Mott "8-N" rule [7], where N is the number of outershell electrons. Nevertheless, the CN(In) is a subject of great controversy where coordinations equal to 1 [8,9], 3 [10,11], 4 [12–14], and 5 [15] have been proposed. Given the diversity of these values and in an attempt to resolve the controversy regarding the CN(In) in this system and to be able to calculate Z for the investigated compositions, we performed [16] extended X-ray absorption fine structure (EXAFS) measurements at the In K-edge. The measurements were performed on a series of glassy samples and on a devitrified $Ge_5Se_{80}In_{15}$ sample. The results showed that In atoms are threefold coordinated with Se atoms only. Therefore, coordination numbers of 4, 2 and 3 for Ge, Se, and In, respectively, are used in the calculation of Z, which is for $Ge_ySe_{94-y}In_6$ given via the relation

$$Z = 2.06 + 0.02y \tag{1}$$

Recently, compositional trends of physicochemical properties such as the free volume percentage [17], compactness [18], density [19], mean atomic volume [20], glass transition temperature [21] and heat capacity jump at T_g [22], for this system, have been reported by us.

In the present work, we report and discuss the composition dependence of the optical band gap, E_g, and cohesive energy (CE) in Ge–Se–In thin films.

2. Experiment

The $Ge_ySe_{94-y}In_6$ bulk materials have been prepared according to the well established melt-quench technique. Appropriate atomic percentages of high purity elements (5 N) are vacuum sealed (10^{-5} Torr) into fused silica tubes of length 80 mm and internal diameter 8 mm. The sealed tubes are then heated in an electric furnace up to 850 °C for 48 h. After complete melting and homogenization, the tubes are quenched in an ice-water mixture to obtain the glass.

Amorphous Ge–Se–In films are obtained by standard vacuum thermal evaporation of Ge–Se–In bulk glasses. Bulk glass with a composition identical to the one of the film is evaporated from an open tungsten boat onto an ultrasonically cleaned glass substrate (microscope slide). The pressure inside the vacuum chamber is maintained at a value lower than 10^{-5} Torr. The substrates are kept at room temperature during the deposition. The source-substrate distance is 10 cm. The films are kept inside the deposition chamber for 24 h to achieve metastable equilibrium. The films are about 120 nm thick and have been measured using a multiple beam interferometer [23].

X-ray diffraction technique is used to check the structure of the prepared samples. The measurements are performed using Mo K_α radiation ($\lambda = 0.71069\,\text{Å}$). The absence of sharp diffraction lines and the presence of humps only confirms the amorphous nature of the prepared samples.

X-ray photoelectron (XPS) spectroscopy is used to determine the chemical compositions of the films and are found to be within $\pm1\%$ to those of the starting bulk glasses. The XPS measurements have been performed using an ESCA spectrometer of Physical Electronics (Perkin–Elmer, PH5600 Ci) with 180° hemispherical analyzer and using monochromotized Al K_α radiation ($hv = 1486.6$ eV).

The absorption spectra of the as-deposited thin films have been measured using a double beam Hitachi UV-Vis-NIR spectrophotometer in the spectral range 250–3000 nm. The spectra have been recorded at normal incidence and at room temperature. The absorption measurements are carried out against a virgin ultrasonically cleaned substrate which served as a reference. They are done in various parts of the films, scanning the entire sample, and the obtained spectra are excellentlally reproduced.

3. Results and discussion

The low-wavelength absorption data are related to interband transitions (i.e excitation of an electron from the valence band to the conduction band). The optical energy gap, E_g, for Ge–Se–In films can be calculated from the well-known quadratic equation [24–27], which is often called Tauc law

$$\alpha hv = A(hv - E_g)^m \tag{2}$$

where hv is the incident photon energy, A is a constant that depends on the electronic transition probability and the exponent m is a parameter which depends on the type of electronic transition responsible for the absorption. Values of $m = 2$ and $m = 0.5$ correspond, respectively, to allowed indirect and allowed direct optical transitions.

In the present work, the plots of $(\alpha hv)^{0.5}$ versus hv for $Ge_ySe_{94-y}In_6$ films ($y = 8$, 22 and 30 at %), depicted in Fig. 1, show good linearity over a wide range of photon energies indicating the allowed indirect type of transition. The other films showed a similar behavior and are not shown to avoid repetition. By extrapolating the linear portion of the curves to zero absorption, the energy gaps are
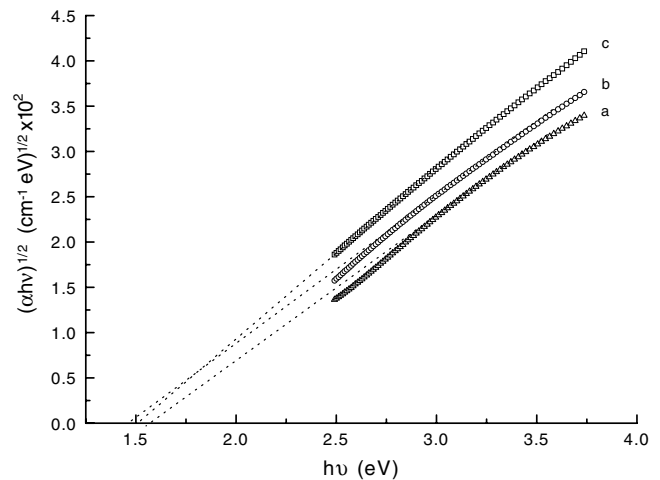

Fig. 1. Tauc's plots for $Ge_ySe_{94-y}In_6$ thin films (a: $y = 22$, b: $y = 8$, c: $y = 30$).

determined. Their values vary from 1.44 to 1.58 eV for films with $y = 8$ and 28.33 at%, respectively. It is worth emphasizing here that the type of optical transition observed in the present work appears to be common in predominantly covalent network thin film systems. It has been observed in binary Ge–Se [28–30], Ge–S [31], As–S [32,33] and As–Se [34]; in ternary Ge–S–Sb [35,36], Ge–Se–Sb [37], Se–Te–Pb [38,39], Ge–As–Se [40–43], Ge–Te–Cu [44], As–Se–Cu [45], Se–Te–Ag [46], As–Te–Ag [47], Zn–Fe–S [48], Ge–Se–Ga [49], Ge–Se–Fe [50], Ge–Se–Te [51], and Ge–Se–Tl [52]; in quaternary Ge–S–Bi(Tl, In) [53]; and in multicomponent As–Se–S–Te–Sn–Ag [54].

The variation of E_g with covalent coordination number, Z, is shown in Fig. 2 where E_g increases up to $Z = 2.63$ and decreases thereafter. A number of factors determine the Z-dependence of E_g in these materials. These are discussed in the following paragraphs.

In chalcogenide glasses, the valence band (σ-bonding) originates from lone-pair (LP) electron states whereas the conduction band arises from antibonding (σ^*) states [55]. The variation of E_g with Z is mainly determined by the composition dependence of three major factors, namely, the bond strengths, the network connectedness and density. From a chemical approach [55], an increase in the bond strengths causes a larger splitting between σ and σ^* bands which results in an increase in E_g. The composition with $Z = 2.63$ has a maximum in E_g at 1.58 eV. This stoichiometric composition is usually referred to as the tie-line composition or the chemical threshold of the system. Its chemical formula can be represented as $(GeSe_2)_{0.85}(In_2Se_3)_{0.15}$. At this composition, the glass structure is made up of completely cross-linked tetrahedral-like $GeSe_2$ and pyramidal-like In_2Se_3 structural units which consist of the energetically favored heteronuclear bonds only. Taking this composition as a reference, glasses with $Z < 2.63$ are chalcogen rich glasses and those with

$Z > 2.63$ are Ge-rich glasses. Because of the fixed amount of In in the films, the number of In–Se bonds is fixed and the variation in the average bond strength is only due to the variation in Se and Ge concentrations in the films. Therefore, the decrease in E_g for Se-rich compositions can be attributed to the progressive replacement of the strong Ge–Se heteronuclear bonds (bond energy = 49.1 kcal/mole) by the weaker homonuclear Se–Se bonds (bond energy = 44.0 kcal/mole). The heteronuclear bond energies are calculated from the bond energies of homonuclear bonds and the electronegativities of the atoms using the formula [56],

$$U(A - B) = 0.5[U_{A-A} + U_{B-B}] + 23(X_A - X_B)^2 \qquad (3)$$

where U_{A-A} and U_{B-B} are the homonuclear bond energies of atoms A and B respectively, and X_A and X_B are their electronegativities. Similarly, the replacement of the strong heteronuclear Ge–Se bonds by the weaker Ge–Ge homonuclear bonds (bond energy = 37.6 kcal/mole), in Ge-rich compositions, lead to the observed decrease in E_g. Thus, from bond energy considerations, there will be a decrease in E_g on both sides of the stoichiometric composition with $Z = 2.63$.

The increase in network connectedness, which is identically equal to Z [57], can lead to an increased interaction between the atomic species, which in turn can widen the seperation between σ and σ^* states and thus increases E_g. Furthermore, the energy of the conduction band edge is decided by N, the number of atoms per unit volume, where a decrease in N leads to an increase in the energy of the conduction band edge and increases E_g. Earlier investigations [19] indicate that the density of Ge–Se–In glasses decreases up to the stoichiometric composition and then increases. The maximum in E_g for the stoichiometric composition is, therefore, a consequence of short-range order effects accompanying the decrease of its density. For $Z > 2.63$, the present results indicate that the appearance of the weak homonuclear Ge–Ge bonds and the increase in N overcome the effect of the increase in network connectedness which causes the overall observed decrease in E_g. Thus, the E_g-Z variation of the Ge–Se–In thin films is consistent with chemical energy considerations, network connectedness, and the compositional variation of density.

The values of E_g of Ge–Se–In [58], Ge–Se–Sb [59], Ge–Se–Ga [60] glasses obtained from data on activation energy for electrical conduction and those obtained on Ge–Se–In glasses using a photoacoustic (PA) technique [61] also exhibit a maximum for the stoichiometric composition. However, a direct comparison between our results and those reported in references [58,61] is not possible because the compositions prepared and the samples investigated (bulk glasses versus thin films in this work) are different. Similar maxima were also reported in Ge–Se bulk glasses [28], Ge–Se thin films [29,30] and Ge–As–Se bulk glasses [43]. For the Ge–Se–In system, the results of measurements on the
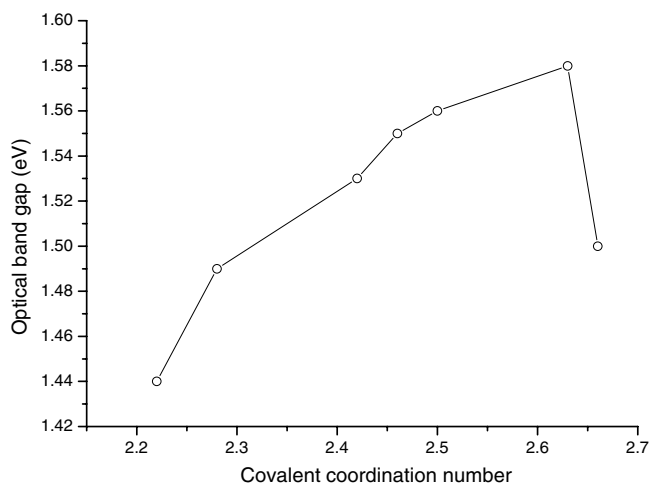

Fig. 2. Variation of the optical band gap with covalent coordination number in $Ge_ySe_{94-y}In_6$ thin films. Solid lines are drawn through data points to guide the eye.

variation with composition of the free volume percentage [17], compactness [18], density [19], mean atomic volume [20], glass transition temperature [21] and heat capacity jump at T_g [22] show extrema at the stoichiometric composition. The above observations are also associated with chemical ordering effects taking place at the stoichiometric composition in the respective systems.

To this end, it would be interesting to calculate the cohesive energy (the stabilization energy of an infinitely large cluster of the material per atom) for the investigated samples and to see if their CE-Z dependence exhibits any peculiar behavior. This is done using the method suggested by the chemical bond approach (CBA) [62]. In view of this method, atoms combine more favorably with atoms of different kinds than with the same kind. This condition is equivalent to assuming the maximum amount of chemical order. Consequently, bonds between like atoms will only ocurr if there is an excess of certain type of atoms. Bonds are formed in the sequence of decreasing bond energies until all the available valences are satisfied.

The relative fraction of the bonds expected to occur in the various samples together with E_g, Z, and CE values are listed in Table 1. In Ge-deficient compositions ($Z < 2.63$), the divalent Se atoms will first saturate the available valences of the tetravalent Ge atoms and then those of the trivalent In atoms [U(In–Se) = 48.2 kcal/mole]. After all these bonds are formed, there are still unsatisfied Se valences, which are satisfied by the formation of Se–Se bonds. Similarly, for Ge-rich compositions ($Z > 2.63$) and after all the available valences of Se and In are saturated, there are still unsaturated Ge valences which must be saturated by the formation of Ge–Ge bonds. According to the CBA, the bond energies are assumed to be additive. Thus, the cohesive energies are calculated by summing the bond energies of the bonds present in the film structure in their relative proportions. The CE-Z variation is presented in Fig. 3. It is seen that the CE passes through a maximum at $Z = 2.63$. The increase of CE of the Ge–Se–In system tends to increase the energy of the conduction band edge causing a larger splitting between σ and σ^* orbitals and thus resulting in the observed increase in E_g. The afterward decrease in CE, for $Z > 2.63$, leads to a decrease in E_g, as observed. It should be mentioned here that the CBA neglects dangling bonds and other valence defects as a first
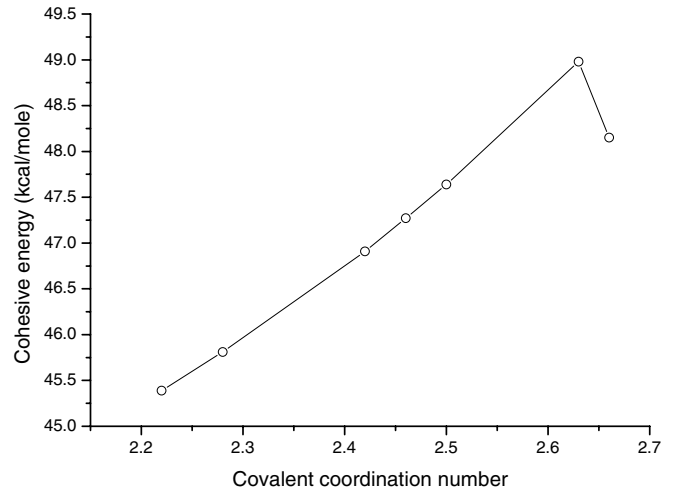

Fig. 3. Variation of the cohesive energy with covalent coordination number in $Ge_ySe_{94-y}In_6$ films. Solid lines are drawn through data points to guide the eye.

approximation. Also, Van der Waals interactions, which can provide means for further stabilization by the formation of much weaker bonds than regular covalent bonds, are neglected.

Other parameters, such as "r", also play an important role in the analysis of the results. This parameter "r", for the samples under investigation, is calculated according to the formula [14]

$$r = \frac{188 - 2y}{4y + 18} \tag{4}$$

The calculated values of "r" are listed in Table 1. The "r" parameter represents the ratio of covalent bonding possibilities of chalcogen atoms to covalent bonding possibilities of non-chalcogenide atoms [14]. Thus $r = 1$ represents the case of the stoichiometric composition, consisting only of the energetically favored heteronuclear bonds, which unequivocally manifest the existence of a chemical threshold. As can be seen from Table 1, E_g and CE attain their maximum values for the composition with $r = 1$. This result lends further support for the validity of the above arguments, which are mainly based on chemical bond considerations, and used for the interpretation of the composition dependence of CE and E_g.

Table 1
Optical band gaps, covalent coordination number, "r" values, distribution of chemical bonds and cohesive energies in $Ge_ySe_{94-y}In_6$ thin films

Film composition (y)	E_g (eV)	Z	r	Distribution of chemical bonds				CE (kcal/mole)
				Ge–Se	In–Se	Se–Se	Ge–Ge	
8	1.44	2.22	3.44	0.1860	0.1047	0.7093	–	45.39
11	1.49	2.28	2.68	0.2651	0.1084	0.6265	–	45.81
18	1.53	2.42	1.69	0.4737	0.1184	0.4079	–	46.91
20	1.55	2.46	1.51	0.5405	0.1217	0.3378	–	47.27
22	1.56	2.50	1.36	0.6111	0.1250	0.2639	–	47.64
28.33	1.58	2.63	1.00	0.8626	0.1374	–	–	48.98
30	1.50	2.66	0.93	0.7971	0.1304	–	0.0725	48.15

4. Conclusions

The E_g-Z and CE-Z dependences of Ge–Se–In thin films exhibit maxima at $Z = 2.63$ which can be understood as a realization of a chemical threshold in these thin films. This Z value lies in the region near to Tanaka's threshold ($Z = 2.67$). It has also been shown that E_g closely correlates with the character of the short-range order. Three factors, the bond strength, the network connectivity, and density are found useful in interpreting the E_g-Z in Ge–Se–In thin films and other chalcogenide thin films.

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