

## THE DISPERSION ENERGIES WEMPLE-DIDOMENICO IN CHALCOGENIDE FILMS BASED ON Ge-As(Sb)-S(Se)

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*The dispersion energies and the single oscillator energies were calculated using the optical transmission data in amorphous chalcogenide films based on Ge-As(Sb)-S(Se). It is shown that the Wemple-DiDomenico refractive-index model can describe the dispersion parameters.*

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### 1. Introduction

S. H. Wemple and M. DiDomenico [1] have analyzed the refractive-index dispersion data below the interband absorption edge in covalent and ionic materials. They have shown that a single-effective-oscillator fit of the form

$$n^2 - 1 = E_d E_o / (E_o^2 - \hbar^2 \omega^2) \quad (1)$$

can be used in a wide range of different solids and liquids. In (1)  $\hbar\omega$  is the photon energy,  $E_o$  is the single oscillator energy and  $E_d$  is the dispersion energy. The latter energy is a measure of the strength of interband optical transitions and it was found to obey the simple empirical relationship

$$E_d = \beta N_c Z_a N_e \quad (2)$$

where  $N_c$  is the co-ordination number of the cation nearest neighbour to the anion,  $Z_a$  is the formal chemical valence of the anion,  $N_e$  is the effective number of valence electrons per anion and  $\beta$  is a parameter between  $0.26 \pm 0.04$  eV (for ionic materials) and  $0.37 \pm 0.05$  eV for covalent materials. It was also found [2] that the mentioned relationships can be applied to a variety of optical glasses and amorphous semiconductors, mainly in tetrahedral materials and mixed-oxide glasses. An example was given also for amorphous  $As_2S_3$ , Se and Te.

In the present investigation the dispersion energies  $E_d$  and  $E_o$  are determined from the experimental results on the optical transmission measurements in thin ternary chalcogenide films. Spectrophotometers SPECORD UV VIS, SPECORD 61 NIR and SHIMADZU were used for the transmission measurements, covering the spectral range of 0.3-2.5  $\mu\text{m}$ . The thickness of the evaporated films was chosen in a way to display 5 to 15 interference extrema in the transmission curves. Then, the method of Swanepoel [3] was used to calculate the refractive index  $n$  and the absorption coefficient  $\alpha$ . The optical band gap  $E_g$  was estimated by the Tauc plot,  $(\alpha\hbar\nu)^{1/2} = f(\hbar\nu)$ . It should be noted that the calculated from this plot  $E_g$  values differ by about 10-20 % from the  $E_g$  estimated from the  $\alpha = f(\hbar\nu)$  dependence at  $\alpha = 10^3 \text{ cm}^{-1}$  or  $10^4 \text{ cm}^{-1}$ . Nevertheless, we think that in the investigated films the Tauc plot is better to be used for the determination of the optical band gap  $E_g$ . The reason of such preference are the observed differences in the shape of the  $\alpha(\hbar\nu)$ -dependencies for different compositions of the same family in one and the same energy range. Furthermore, the calculated  $\alpha$  were in the range of  $10^3 \text{ cm}^{-1}$  to  $10^4 \text{ cm}^{-1}$ , i.e. the range of values where the Tauc plot is regularly used.

Once the refractive index obtained, the energies  $E_d$  and  $E_o$  were calculated by means of the plot of  $1/(n^2-1)$  versus  $\lambda^{-2}$  [1]. In fact the dispersion energies were calculated using a computer program which simulated the mentioned plot on the basis of a lot of  $(n, \lambda)$  pairs.

## 2. Materials and experimental methods

After the discovery of the semiconducting lasses by N. Goryunova and B. Kolomiets in the early '50, the chalcogenide semiconductors have been widely investigated around the world. Many topics - properties and materials - have attracted the attention of the scientists in different time periods. The most frequently investigated materials have been the binary vitreous and amorphous compounds:  $As_2S_3$ ,  $As_2Se_3$ ,  $GeS_2$  and  $GeSe_2$ . The ternary Ge-As-S(Se) systems are also interesting because of their high glass-forming tendency. In these systems the  $As_2S(Se)_3$ -Ge composition line was investigated in details in the Institute of Applied Physics, Moldova, under the leadership of Prof. Andrei Andriesh in Moldova [4]. The  $As(Sb)_2S(Se)_3$ - $GeSe_2$  lines were investigated by the scientists from Pardubice (the group of Prof. L. Tichý, Prof. M. Frumar and collab.). The  $As(Sb)_2S(Se)_3$ - $GeS(Se)_{1.5}$  composition lines, containing one stoichiometric and one non-stoichiometric component, were mainly investigated by the laboratory of Prof. E. Vateva in Sofia [5, 6]. The object of the present investigation is thin films of the last mentioned type, evaporated from  $Ge_xAs_{40-x}Se(S)_{60}$  glasses. Some data on Sb- instead of As- containing compounds are presented, as well as several data obtained from thin films from the As-Se system.

The glasses were prepared by the common melt-quenching method. The thin films have been prepared by thermal evaporation. Usually, thin chalcogenide films are evaporated at a rate  $\sim 1$  nm/s. In order to obtain thin Ge-As(Sb)-Se(S) films with a composition near that of the parent glass an evaporation rate of 7-10 nm/s was used. The composition of the films evaporated in these conditions showed little difference from that of the parent glass as checked by a microsonde method. The thickness of the films (0.5-2.5  $\mu m$ ) and the evaporation rate were controlled *in situ*.

The Wemple-DiDomenico dispersion parameters  $E_d$  and  $E_o$  for the chalcogenide films were calculated from the optical experimental data and compared with those determined in other materials.

## 3. Results and discussion

It is well known that glasses, exhibit the same short-range order as the corresponding crystals, but are lacking long-range order. The structure and the properties of the disordered materials are very sensitive to preparation techniques and, as a rule, the structure of the evaporated films is more disordered than that of the parent glasses. In addition, the investigated materials are complex compounds, which contain two types of the main structural units (SU) – e.g.  $As_2S_3$ -pyramids and  $GeS_2$ -tetrahedra – interconnected in between. In such films one can use most of the characteristic parameters only in an averaged form. The optical measurements were performed using a light beam through the 22-mm length of the sample and therefore the experimental data provided the necessary mean values. Hence the obtained  $E_d$  and  $E_o$  are also average values. Moreover, the use of the experimental  $n$  values could lead to certain error in view of the dependence of the calculated refractive index on the thickness of the investigated film. However, this dependence is relatively weak. The results cited in Table 1 and Table 2 are obtained from films with thickness about 1.5  $\mu m$ . Only the films from the As-Se system were 2-3  $\mu m$  thick while the  $GeSe_{1.5}$  films were about 1  $\mu m$ .

In Table 1,  $\langle m \rangle$  is the average coordination number of the parent glass composition.  $E_d$  and  $E_o$  are the Wemple-DiDomenico dispersion energies,  $E_g$  is the optical band gap,  $n_o$  is the value of the refractive index extrapolated to  $\omega=0$  ( $\lambda=\infty$ ) [3] and  $\Delta=1-E_d/E_o(n_o^2-1)$ .  $\Delta$  may be regarded as a measure of the accuracy and, hence, of the homogeneity of the investigated films. For instance, in the As-Se system,  $\Delta$  is very large because it was very difficult to obtain good (homogeneous and transparent)  $As_3Se_2$  and  $AsSe$  films in our preparation procedure.

Table 1. The dispersion energies and refractive indices in some chalcogenide films.

| Composition  | $\langle m \rangle$ | $E_d$ , eV | $E_o$ , eV | $E_g$ , eV | $n_o(\lambda=\infty)$ | $\Delta$ , % |
|--|---------------------|------------|------------|------------|-----------------------|--------------|
| As <sub>60</sub> Se <sub>40</sub>                  | 2.6                 | 29.6       | 5.9        | 1.89       | 2.64                  | 15.9         |
| As <sub>50</sub> Se <sub>50</sub>                  | 2.5                 | 29         | 5.7        | 1.83       | 2.625                 | 13.5         |
| As <sub>40</sub> Se <sub>60</sub>                  | 2.4                 | 28         | 4.7        | 1.75       | 2.58                  | 7.19         |
| Ge <sub>5</sub> As <sub>35</sub> Se <sub>60</sub>  | 2.45                | 23         | 4.1        | 1.736      | 2.548                 | 2.18         |
| Ge <sub>10</sub> As <sub>30</sub> Se <sub>60</sub> | 2.5                 | 23.2       | 4.5        | 1.752      | 2.554                 | 6.6          |
| Ge <sub>15</sub> As <sub>25</sub> Se <sub>60</sub> | 2.55                | 23.8       | 4.4        | 1.787      | 2.565                 | 3.1          |
| Ge <sub>19</sub> As <sub>21</sub> Se <sub>60</sub> | 2.59                | 22         | 4.36       | 1.76       | 2.45                  | 1            |
| Ge <sub>22</sub> As <sub>18</sub> Se <sub>60</sub> | 2.62                | 22.2       | 4.44       | 1.804      | 2.443                 | 0.6          |
| Ge <sub>25</sub> As <sub>15</sub> Se <sub>60</sub> | 2.65                | 23.8       | 4.65       | 1.795      | 2.47                  | 0.4          |
| Ge <sub>28</sub> As <sub>12</sub> Se <sub>60</sub> | 2.68                | 22         | 4.3        | 1.79       | 2.48                  | 0.6          |
| Ge <sub>32</sub> As <sub>8</sub> Se <sub>60</sub>  | 2.72                | 22.6       | 4.46       | 1.76       | 2.462                 | 1.9          |
| Ge <sub>36</sub> As <sub>4</sub> Se <sub>60</sub>  | 2.76                | 24.2       | 4.6        | 1.653      | 2.44                  | 6.3          |
| Ge <sub>40</sub> Se <sub>60</sub>                  | 2.8                 | 16         | 3.7        | 1.48       | 2.255                 | 5.7          |
| Ge <sub>10</sub> Sb <sub>30</sub> Se <sub>60</sub> | 2.5                 | 20.2       | 3.5        | 1.32       | 2.61                  | 0.7          |
| Ge <sub>15</sub> Sb <sub>25</sub> Se <sub>60</sub> | 2.55                | 23         | 3.5        | 1.41       | 2.81                  | 4.7          |
| Ge <sub>25</sub> Sb <sub>15</sub> Se <sub>60</sub> | 2.65                | 23.3       | 4.1        | 1.518      | 2.64                  | 4.8          |
| Ge <sub>27</sub> Sb <sub>13</sub> Se <sub>60</sub> | 2.67                | 23.5       | 4.35       | 1.53       | 2.53                  | 0            |
| Ge <sub>32</sub> Sb <sub>8</sub> Se <sub>60</sub>  | 2.72                | 22.5       | 4.1        | 1.56       | 2.55                  | 0.1          |
| Ge <sub>35</sub> Sb <sub>5</sub> Se <sub>60</sub>  | 2.75                | 20.4       | 3.8        | 1.512      | 2.533                 | 0.8          |

The energies  $E_d$  and  $E_o$  values are of the same order of magnitude as those already published [1,2]. In a given system  $E_o$  could be regarded as constant. In the Ge-As-Se system one can hardly see any dependence on the composition. This behavior could be related to the observation regarding the small compositional differences between the film and the parent glass. The microsonde measurements have shown that these differences are in the range of 2-3%. On the other hand, Raman scattering [8] and infrared optical measurements [5, 9] have shown that in the spectra of Ge<sub>x</sub>As<sub>40-x</sub>S<sub>60</sub> thin films and glasses the position of the bands are the same for a given  $x$  and only their integrated areas differ appreciably. The relative part of the SU with "wrong" bonds in the films is greater. That is why the scattering in the compositional dependence of  $E_d$  is due not to deviations in the composition but to structural disorder.

Popescu [10] has proposed a preliminary model of the SU distribution in thin Ge<sub>x</sub>As<sub>40-x</sub>Se<sub>60</sub> films fitted to various experimental results including microhardness data. The model takes into account (besides the regular As<sub>2</sub>Se<sub>3</sub>-pyramids and GeSe<sub>2</sub>-tetrahedra), the presence of As<sub>4</sub>S<sub>4</sub> and GeSe SU. The latter appear in the film matrix in different amount for different  $x$ . The appearance of new structural units, even in a small amount, leads to an increase of the disorder [11]. On the basis of the Raman spectra measured on Ge<sub>x</sub>As<sub>40-x</sub>S<sub>60</sub> films one can suggest that in the structure of the films appears a great amount of SU with greater and/or smaller coordination than the regular SU. The same situation should also be present in the Se-containing films. Hence, in the materials discussed above,  $\beta$ ,  $N_c$  and  $N_e$  in (2) should be very complex. For instance, the nearest neighbors could be different not only in different compositions, but also in different parts of the sample. Nevertheless, we can admit that, *grasso modo*, even in the disordered amorphous films similar to the investigated ones, the dispersion energy  $E_d$  obeys the relationship (2).

In the Ge-Sb-Se system the situation is to some extent better: As in the case of  $E_g$ ,  $E_d$  is also slightly dependent on the composition. The expected increase of  $E_d$  because of the increase of the ionicity when Sb replaces As however is not detectable. This is probably due to technological reasons: the Ge-Sb- chalcogenides show a higher decomposition rate than the Ge-As- chalcogenides, when heated. The values obtained in the present investigation differ from those calculated for the same system in the literature [7]. Viček et al. [7] concluded that  $E_d$  is expected to change gradually from 21.92 to 20.78 eV in the range  $12 < x < 40$ . However, their data are related to glasses. Constant  $\beta$ ,  $N_c$  and  $Z_o$  are used and  $N_e$  is calculated by a rather simple formula.

The comparison between the dispersion parameters of several amorphous semiconductors and of the corresponding crystals [2] has shown that  $E_d$  decreases by the amorphization. This fact, assigned to a decrease in oscillator strength of lone-pair to conduction-band transitions, occurs probably also in the investigated materials.

Table 2 Influence of the annealing on the Wemple-DiDomenico energies in  $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$  thin films.

| Composition                                 | $E_d$ , eV |          | $E_o$ , eV |          | $\Delta E_d/E_d$ , % | $\Delta E_g/E_g$ , % |
|---|------------|----------|------------|----------|----------------------|----------------------|
|   | (Fresh)    | Annealed | (Fresh)    | Annealed |                      |                      |
| $\text{As}_{40}\text{S}_{60}$               | 24.1       | 25.2     | 6          | 6        | 4.5                  | -1.7                 |
| $\text{Ge}_4\text{As}_{36}\text{S}_{60}$    | 24.8       | 25.7     | 5.9        | 6.5      | 3.6                  | 1.5                  |
| $\text{Ge}_{11}\text{As}_{29}\text{S}_{60}$ | 24.7       | 25       | 5.9        | 6.3      | 1.2                  | 5.26                 |
| $\text{Ge}_{15}\text{As}_{25}\text{S}_{60}$ | 24.6       | 26.4     | 5.8        | 6.5      | 7                    | 7.5                  |
| $\text{Ge}_{22}\text{As}_{18}\text{S}_{60}$ | 24.4       | 26.5     | 6.1        | 6.2      | 8.6                  | 10.3                 |
| $\text{Ge}_{25}\text{As}_{15}\text{S}_{60}$ | 24.6       | 26.8     | 6          | 6.4      | 8.9                  | 13.2                 |
| $\text{Ge}_{28}\text{As}_{12}\text{S}_{60}$ | 24.3       | 25.9     | 5.85       | 6        | 6.6                  | 14.8                 |
| $\text{Ge}_{36}\text{As}_4\text{S}_{60}$    | 26.2       | 27.4     | 5.9        | 6.3      | 4.6                  | 13.8                 |

The fresh (evaporated) films are usually highly disordered. Annealing of the film results in a relative increase of the structural order and partial reconnection of the atomic and molecular bonds. After annealing, many properties of the thin films are changed, including the optical parameters. The change of the refractive index after annealing leads to changes in the  $E_d$  and  $E_o$  values. An example is given in Table 2 for Ge-As-S thin films. The samples were annealed in Ar-atmosphere at temperatures about 30° below the glass-transition temperatures of the parent glasses. As could be expected [1,2]  $E_o$  is almost the same in all of the compositions and does not change significantly after annealing. The dispersion energy  $E_d$  slightly increases with the co-ordination number as shown in [2]. The ordering of the film structure leads also to  $E_d$  increase. This increase is only of several percents and its compositional dependence is similar to that of the optical band gap. In the last case two exceptions must be pointed out (i) for  $\text{As}_{40}\text{S}_{60}$  which is thermo-darkened while all other compositions are thermo-bleached and (ii) for  $\text{Ge}_{36}\text{As}_4\text{S}_{60}$  which is the most disordered. Raman investigations of fresh and annealed films and bulk glasses of the same family [8] have shown that the annealed films are more ordered than the fresh ones but the degree of ordering of the parent glass can not be reached. That is why  $E_d$  remains relatively low even in the annealed films. For comparison  $E_d=33$  eV for crystalline  $\text{As}_2\text{S}_3$  [2]. The difference for  $E_d$  of the amorphous  $\text{As}_2\text{S}_3$  ( $E_d=22.8$  eV in [2]) is probably due to technological differences.)

#### 4. Conclusions

The dispersion energy,  $E_d$ , and the single oscillator energy,  $E_o$ , were calculated from the data of optical transmission measurements in thin Ge-As(Sb)- chalcogenide films. It was found that even in the case of ternary amorphous films with complex short and medium range order the dispersion parameters can be described by the Wemple-DiDomenico refractive-index model. In the amorphous films  $E_d$  could also obey the relationship (2).

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the Swanepoel's method for the calculation of the optical parameters of the films. Thanks also to E. Savova for providing the Ge-Sb-Se films.

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