

# Compositional dependence of the optical constants of amorphous $\text{Ge}_x\text{As}_{20}\text{Se}_{80-x}$ thin films

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## Abstract

This paper reports the effect of replacement of selenium by germanium on the optical constants of chalcogenide  $\text{Ge}_x\text{As}_{20}\text{Se}_{80-x}$  (where  $x = 0, 5, 10, 15$  and  $20$  at.%) thin films. Films of  $\text{Ge}_x\text{As}_{20}\text{Se}_{80-x}$  glasses were prepared by thermal evaporation of the bulk samples. The transmission spectra,  $T(\lambda)$ , of the films at normal incidence were obtained in the spectral region from  $400$  to  $2500$  nm. A straightforward analysis proposed by Swanepoel, based on the use of the maxima and minima of the interference fringes, has been applied to derive the real and imaginary parts of the complex index of refraction and also the film thickness. Increasing germanium content is found to affect the refractive index and the extinction coefficient of the  $\text{Ge}_x\text{As}_{20}\text{Se}_{80-x}$  films. Optical absorption measurements show that the fundamental absorption edge is a function of composition. With increasing germanium content the refractive index decreases while the optical band gap increases.

## 1. Introduction

Structural, optical and photoelectronic properties of chalcogenide amorphous thin films have been the subject of interest for many years [1–3]. This interest has been stimulated both by basic scientific questions that have to be answered in order to understand the structure and properties of these non-crystalline materials and by the need to assess their potential technological applications. Chalcogenide films have some unique properties, such as high values of refractive indices and transparency in middle and far infrared parts of the electromagnetic spectrum, that make them attractive for different applications in optoelectronics [4].

Methods for determining the optical constants of the chalcogenide amorphous thin films, based exclusively on the optical transmission spectra at normal incidence, have been made [5–8]. These relatively simple methods do not require any previous knowledge of the thickness of the films and are fairly accurate with the thickness and refractive index being determinable to within about 1% [5]. They do, however,

assume that the film has a uniform thickness which, when absent, leads to less accurate results and even serious errors.

This paper is concerned with the analysis of the optical properties of as-deposited amorphous  $\text{Ge}_x\text{As}_{20}\text{Se}_{80-x}$  (where  $x = 0, 5, 10, 15$  and  $20$  at.%) thin films, prepared by thermal evaporation. A straightforward method was proposed by Swanepoel [5], which is based on the use of maxima and minima of the interference fringes in the transmission spectrum for calculation of the refractive index and film thickness in the weakly absorbing and transparent regions of the spectrum. The absorption coefficient, and therefore the extinction coefficient, has been determined from transmission spectra in the strong absorption region. Although it is possible to find in the literature some papers dealing with both bulk and thin films [9, 10] within this composition line, to the best of our knowledge, there is no thorough study of its optical properties. Therefore, the lack of data in the literature concerning the optical characterization of films of these particular materials, along with their attractive potential technological applications, highlights the significance of the present investigation.

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## 2. Experimental details

Different compositions of bulk  $\text{Ge}_x\text{As}_{20}\text{Se}_{80-x}$  (where  $x = 0, 5, 10, 15$  and  $20$  at.%) chalcogenide glasses were prepared from their components of high purity (99.999%) by the melt quenching technique. The elements were heated together in an evacuated ( $10^{-3}$  Pa) silica ampoule up to 1175 K and then the ampoule temperature was kept constant for about 24 h. During the course of heating, the ampoule was shaken several times to maintain the uniformity of the melt. Finally, the ampoule was quenched into ice cooled water to avoid crystallization.

Thin films of  $\text{Ge}_x\text{As}_{20}\text{Se}_{80-x}$  were prepared by thermal evaporation of the bulk samples. The thermal evaporation process was performed inside a coating (Edward 306E) system, at a pressure of approximately  $10^{-3}$  Pa. During the deposition process (at normal incidence), the substrates were suitably rotated in order to obtain films of uniform thickness. According to Kosa *et al* [11], the homogeneity of the studied films was clearly confirmed by the corresponding spectral dependence of transmission, where no shrinkage of the interference fringes was observed.

The elemental compositions of the investigated specimens were checked using energy dispersive x-ray (Link Analytical Edx) spectroscopy. The deviations in the elemental compositions of the evaporated thin films from their initial bulk specimens were found to be  $\pm 1.0$  at.%. The amorphous state of the films was checked using an x-ray (Philips type 1710 with Cu as a target and Ni as a filter,  $\lambda = 1.5418 \text{ \AA}$ ) diffractometer. The absence of crystalline peaks confirms the amorphous state of the prepared samples.

A double beam (Jasco V-630) spectrophotometer was used to measure the transmittance for the prepared films in the spectral range of wavelength from 400 to 2500 nm. Without a glass substrate in the reference beam, the measured transmittance spectra were used to calculate the optical constants of the films. In this work, the envelope method suggested by Swanepoel [5] has been applied.

## 3. Results and discussion

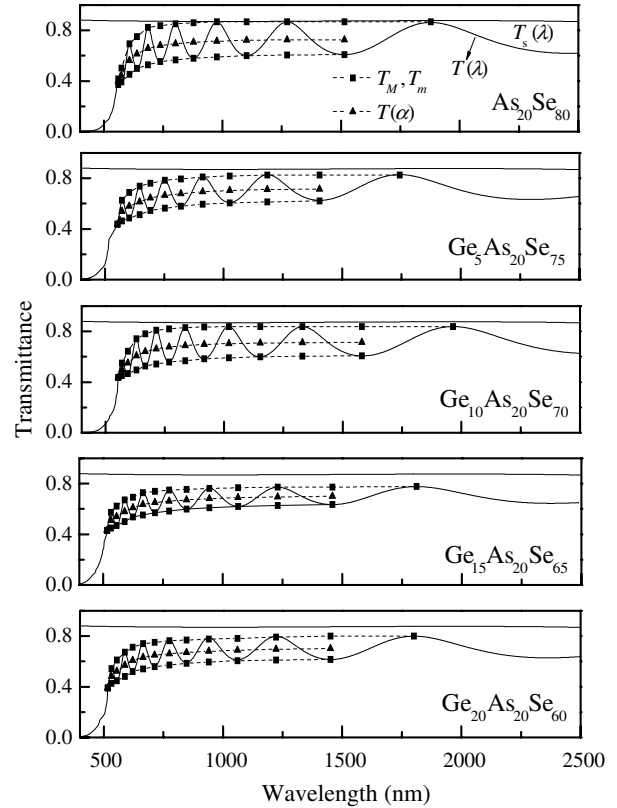
### 3.1. Calculation of the refractive index and film thickness

Figure 1 shows the measured transmittance,  $T$ , spectra, the created envelopes  $T_M$  and  $T_m$  and the geometric mean,  $T_\alpha = \sqrt{T_M T_m}$ , in the spectral region with interference fringes for the  $\text{Ge}_x\text{As}_{20}\text{Se}_{80-x}$  (where  $x = 0, 5, 10, 15$  and  $20$  at.%) thin films, according to Swanepoel's method based on the idea of Manificier *et al* [12]. The first approximate value of the refractive index of the film,  $n_1$ , in the spectral region of medium and weak absorption can be calculated from the following expression:

$$n_1 = \sqrt{N + \sqrt{N^2 - s^2}}, \quad (1)$$

where

$$N = 2s \frac{T_M - T_m}{T_M T_m} + \frac{s^2 + 1}{2},$$



**Figure 1.** Transmission spectra of  $\text{Ge}_x\text{As}_{20}\text{Se}_{80-x}$  (where  $x = 0, 5, 10, 15$  and  $20$  at.%) thin films. The average thicknesses of these samples are 723 nm, 772 nm, 708 nm, 753 nm and 789 nm for  $x = 0$  at.%, 5 at.%, 10 at.%, 15 at.% and 20 at.%, respectively. Curves  $T_M$ ,  $T_m$  and  $T_\alpha$  according to the text.  $T_s$  is the transmission of the substrate alone.

where  $T_M$  and  $T_m$  are the transmission maximum and the corresponding minimum at a certain wavelength  $\lambda$ ; alternatively, one of these values is an experimental interference maximum (minimum) and the other one is derived from the corresponding envelope. Both envelopes were computer-generated using the OriginLab (version 7) program and compared with the computer algorithm developed by McClain *et al* [13]. It is found that the two methods have the same results. The index of refraction of the substrate,  $s$ , at each wavelength is derived from the value of its transmission,  $T_s(\lambda)$  [14]. The calculated values of the refractive index,  $n_1$ , using equation (1) are listed in table 1. The accuracy of this initial estimation of the refractive index is improved after calculating the thickness of the film,  $d$ , as will be explained below. Now it is necessary to take into account the basic equation for the interference fringes:

$$2nd = m_o \lambda, \quad (2)$$

where the order number,  $m_o$ , is an integer for maxima and a half-integer for minima. Moreover, if  $n_{c1}$  and  $n_{c2}$  are the refractive indices at two adjacent maxima (or minima) at  $\lambda_1$  and  $\lambda_2$ , then the film thickness can be expressed as

$$d = \frac{\lambda_1 \cdot \lambda_2}{2(n_{c2}\lambda_1 - n_{c1} \cdot \lambda_2)}. \quad (3)$$

**Table 1.** Values of  $\lambda$ ,  $T_s$ ,  $T_M$ ,  $T_m$ ,  $n_1$ ,  $d_1$ ,  $m_o$ ,  $d_2$  and  $n_2$  for  $\text{Ge}_x\text{As}_{20}\text{Se}_{80-x}$  (where  $x = 0, 5, 10, 15$  and  $20$  at%) thin films from transmission spectra. The underlined values of transmittance are those given in the transmittance spectra of figure 1 and the others are calculated by the envelope method.

| Composition  | $\lambda$  | $s$   | $T_M$        | $T_m$        | $n_1$ | $d_1$ | $m_o$ | $m$ | $d_2$ | $n_2$ |
|--|--|-------|--------------|--------------|-------|-------|-------|-----|-------|-------|
| As <sub>20</sub> Se <sub>80</sub>  | 1514   | 1.706 | 0.865        | <u>0.606</u> | 2.619 |       | 2.49  | 2.5 | 722   | 2.618 |
|  | 1272   | 1.716 | <u>0.864</u> | 0.603        | 2.638 |       | 2.98  | 3   | 723   | 2.639 |
|  | 1102   | 1.720 | <u>0.865</u> | <u>0.599</u> | 2.660 | 731   | 3.47  | 3.5 | 725   | 2.667 |
|  | 976  | 1.722 | <u>0.865</u> | <u>0.587</u> | 2.707 | 714   | 3.99  | 4   | 721   | 2.700 |
|  | 878  | 1.721 | 0.858        | <u>0.579</u> | 2.725 | 724   | 4.46  | 4.5 | 724   | 2.732 |
|  | 802  | 1.717 | <u>0.850</u> | <u>0.564</u> | 2.769 | 736   | 4.96  | 5   | 723   | 2.773 |
|  | 738  | 1.716 | 0.835        | <u>0.552</u> | 2.789 | 740   | 5.43  | 5.5 | 727   | 2.807 |
|  | 686  | 1.713 | <u>0.820</u> | <u>0.525</u> | 2.877 | 675   | 6.03  | 6   | 715   | 2.846 |
|  | 640  | 1.710 | 0.750        | <u>0.497</u> | 2.865 | 717   | 6.44  | 6.5 | 726   | 2.877 |
|  | $\bar{d}_1 = 719, \delta_1 = 22 \text{ nm (3\%); } \bar{d}_2 = 723, \delta_1 = 3.52 \text{ nm (0.484\%)}$  |       |              |              |       |       |       |     |       |       |
| Ge <sub>5</sub> As <sub>20</sub> Se <sub>75</sub>  | 1580   | 1.704 | 0.837        | <u>0.606</u> | 2.562 |       | 2.52  | 2.5 | 770   | 2.558 |
|  | 1330   | 1.714 | <u>0.837</u> | 0.603        | 2.584 |       | 3.02  | 3   | 772   | 2.584 |
|  | 1152   | 1.719 | 0.838        | <u>0.599</u> | 2.607 | 779   | 3.52  | 3.5 | 773   | 2.611 |
|  | 1020   | 1.721 | <u>0.838</u> | <u>0.590</u> | 2.644 | 769   | 4.03  | 4   | 771   | 2.642 |
|  | 916  | 1.721 | 0.834        | <u>0.582</u> | 2.668 | 768   | 4.53  | 4.5 | 772   | 2.670 |
|  | 836  | 1.720 | <u>0.829</u> | 0.568        | 2.715 | 763   | 5.05  | 5   | 769   | 2.707 |
|  | 768  | 1.717 | <u>0.819</u> | <u>0.558</u> | 2.735 | 772   | 5.53  | 5.5 | 772   | 2.736 |
|  | 714  | 1.715 | <u>0.809</u> | <u>0.541</u> | 2.786 | 763   | 6.06  | 6   | 768   | 2.775 |
|  | 668  | 1.712 | 0.780        | <u>0.525</u> | 2.796 | 799   | 6.51  | 6.5 | 776   | 2.812 |
|  | 630  | 1.709 | <u>0.740</u> | <u>0.495</u> | 2.852 | 799   | 7.04  | 7   | 773   | 2.856 |
| $\bar{d}_1 = 777, \delta_1 = 15 \text{ nm (2.1\%); } \bar{d}_2 = 772, \delta_1 = 2.27 \text{ nm (0.29\%)}$ |  |       |              |              |       |       |       |     |       |       |
| Ge <sub>10</sub> As <sub>20</sub> Se <sub>70</sub>   | 1404   | 1.711 | 0.824        | <u>0.618</u> | 2.495 |       | 2.49  | 2.5 | 703   | 2.479 |
|  | 1184   | 1.719 | <u>0.823</u> | 0.611        | 2.528 |       | 3.00  | 3   | 702   | 2.508 |
|  | 1026   | 1.721 | 0.815        | <u>0.603</u> | 2.538 | 717   | 3.48  | 3.5 | 707   | 2.536 |
|  | 912  | 1.721 | <u>0.808</u> | <u>0.593</u> | 2.558 | 746   | 3.94  | 4   | 713   | 2.576 |
|  | 820  | 1.719 | 0.792        | <u>0.578</u> | 2.590 | 730   | 4.44  | 4.5 | 712   | 2.606 |
|  | 752  | 1.717 | <u>0.783</u> | <u>0.561</u> | 2.641 | 707   | 4.94  | 5   | 711   | 2.655 |
|  | 692  | 1.713 | <u>0.759</u> | <u>0.545</u> | 2.657 | 733   | 5.39  | 5.5 | 716   | 2.688 |
|  | 646  | 1.710 | <u>0.735</u> | <u>0.51</u>  | 2.775 | 638   | 6.04  | 6   | 698   | 2.737 |
|  | 602  | 1.707 | 0.687        | <u>0.484</u> | 2.774 | 650   | 6.48  | 6.5 | 705   | 2.763 |
|  | $\bar{d}_1 = 703, \delta_1 = 42 \text{ nm (6.0\%); } \bar{d}_2 = 708, \delta_1 = 5.94 \text{ nm (0.84\%)}$ |       |              |              |       |       |       |     |       |       |
| Ge <sub>15</sub> As <sub>20</sub> Se <sub>65</sub>   | 1450   | 1.709 | 0.797        | <u>0.614</u> | 2.447 |       | 2.56  | 2.5 | 740   | 2.407 |
|  | 1222   | 1.717 | <u>0.789</u> | 0.609        | 2.456 |       | 3.04  | 3   | 746   | 2.434 |
|  | 1060   | 1.721 | 0.780        | <u>0.604</u> | 2.458 | 791   | 3.51  | 3.5 | 754   | 2.463 |
|  | 940  | 1.721 | <u>0.775</u> | <u>0.594</u> | 2.488 | 784   | 4.01  | 4   | 755   | 2.497 |
|  | 846  | 1.720 | <u>0.767</u> | <u>0.584</u> | 2.509 | 773   | 4.49  | 4.5 | 758   | 2.528 |
|  | 774  | 1.718 | <u>0.761</u> | <u>0.571</u> | 2.549 | 774   | 4.99  | 5   | 759   | 2.570 |
|  | 712  | 1.715 | 0.749        | <u>0.558</u> | 2.575 | 767   | 5.48  | 5.5 | 760   | 2.600 |
|  | 664  | 1.712 | <u>0.738</u> | <u>0.538</u> | 2.639 | 734   | 6.02  | 6   | 754   | 2.645 |
|  | 620  | 1.708 | 0.710        | <u>0.518</u> | 2.660 | 741   | 6.49  | 6.5 | 757   | 2.676 |
|  | 588  | 1.706 | <u>0.670</u> | <u>0.480</u> | 2.750 | 711   | 7.08  | 7   | 748   | 2.733 |
| 554  | 1.702  | 0.608 | <u>0.446</u> | 2.753        | 737   | 7.52  | 7.5   | 754 | 2.759 |       |
| $\bar{d}_1 = 757, \delta_1 = 27 \text{ nm (3.6\%); } \bar{d}_2 = 753, \delta_1 = 6.13 \text{ nm (0.81\%)}$ |  |       |              |              |       |       |       |     |       |       |
| Ge <sub>20</sub> As <sub>20</sub> Se <sub>60</sub>   | 1458   | 1.709 | 0.773        | <u>0.634</u> | 2.304 |       | 2.47  | 2.5 | 791   | 2.310 |
|  | 1230   | 1.717 | <u>0.771</u> | 0.626        | 2.340 |       | 2.97  | 3   | 788   | 2.338 |
|  | 1064   | 1.721 | <u>0.767</u> | <u>0.619</u> | 2.361 | 782   | 3.47  | 3.5 | 788   | 2.360 |
|  | 944  | 1.721 | <u>0.762</u> | 0.608        | 2.395 | 787   | 3.96  | 4   | 788   | 2.393 |
|  | 848  | 1.720 | 0.755        | <u>0.598</u> | 2.418 | 791   | 4.45  | 4.5 | 789   | 2.418 |
|  | 776  | 1.718 | <u>0.749</u> | <u>0.584</u> | 2.461 | 788   | 4.95  | 5   | 788   | 2.459 |
|  | 716  | 1.715 | 0.738        | <u>0.571</u> | 2.487 | 803   | 5.42  | 5.5 | 791   | 2.496 |
|  | 666  | 1.712 | <u>0.727</u> | <u>0.553</u> | 2.537 | 782   | 5.95  | 6   | 787   | 2.532 |
|  | 624  | 1.709 | <u>0.693</u> | <u>0.535</u> | 2.525 | 872   | 6.32  | 6.5 | 803   | 2.570 |
|  | 590  | 1.706 | <u>0.671</u> | <u>0.499</u> | 2.646 | 741   | 7.00  | 7   | 780   | 2.617 |
| 556  | 1.703  | 0.622 | <u>0.469</u> | 2.657        | 682   | 7.46  | 7.5   | 784 | 2.643 |       |
| $\bar{d}_1 = 781, \delta_1 = 50 \text{ nm (6.4\%); } \bar{d}_2 = 789, \delta_1 = 5.64 \text{ nm (0.72\%)}$ |  |       |              |              |       |       |       |     |       |       |

The values of  $d$  determined by this equation for different samples are listed as  $d_1$  in table 1. The last value deviates considerably from the other values and must consequently be rejected. The average value,  $\bar{d}_1$ , of  $d_1$  (ignoring the last value),

can now be used, along with  $n_1$  to calculate  $m_o$  for the different maxima and minima using equation (2). The accuracy of the film thickness can now be significantly increased by taking the corresponding exact integer or half-integer values of  $m_o$

associated with each extreme point (see figure 1) and deriving a new thickness,  $d_2$ . The values of the thickness in this way have a smaller dispersion. It should be emphasized that the accuracy of the final thickness is better than 1% (see table 1).

With the accurate values of  $m_0$  and the average value  $\bar{d}_2$  of  $d_2$ , expression (2) can then be solved for  $n$  at each  $\lambda$  and, thus, the final values of the refractive index,  $n_2$ , are obtained. These values are listed in table 1.

Figure 2 illustrates the dependence of the refractive index,  $n$ , on the wavelength for different compositions of the amorphous  $\text{Ge}_x\text{As}_{20}\text{Se}_{80-x}$  (where  $x = 0, 5, 10, 15$  and  $20$  at.%) thin films. Now the values of  $n_2$  can be fitted to a function such as the two-term Cauchy dispersion relationship [15]:

$$n(\lambda) = a + \frac{b}{\lambda^2}, \quad (4)$$

which can then be used to extrapolate the wavelength dependence beyond the range of measurement (see figure 2). This figure shows that the refractive index decreases with increasing Ge content over the entire spectral range studied. The least-squares fit of  $n_2$  for the different samples listed in table 1 yields  $n = 2.56 + (1.37 \times 10^5/\lambda^2)$ ,  $n = 2.51 + (1.38 \times 10^5/\lambda^2)$ ,  $n = 2.416 + (1.30 \times 10^5/\lambda^2)$ ,  $n = 2.346 + (1.28 \times 10^5/\lambda^2)$  and  $n = 2.253 + (1.23 \times 10^5/\lambda^2)$  for  $x = 0$  at.%, 5 at.%, 10 at.%, 15 at.% and 20 at.%, respectively.

The final values of the refractive index can be fitted to an appropriate function such as the Wemple–DiDomenico (WDD) dispersion relationship [16], i.e. to the single-oscillator model:

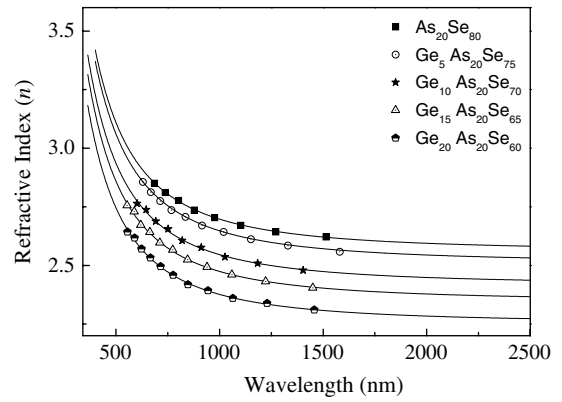
$$n^2(h\nu) = 1 + \frac{E_o E_d}{E_o^2 - (h\nu)^2}, \quad (5)$$

where  $E_o$  is the single-oscillator energy and  $E_d$  is the dispersion energy or single-oscillator strength. By plotting  $(n^2 - 1)^{-1}$  against  $(h\nu)^2$  and fitting straight lines as shown in figure 3,  $E_o$  and  $E_d$  can be determined from the intercept,  $E_o/E_d$ , and the slope,  $(E_o E_d)^{-1}$ . The oscillator energy,  $E_o$ , is an average energy gap and to a good approximation scales with the optical band gap,  $E_o \approx 2E_g$ , as was found by Tanaka [17]. Figure 3 also shows the values of the refractive index  $n(0)$  at  $h\nu = 0$  for the  $\text{Ge}_x\text{As}_{20}\text{Se}_{80-x}$  (where  $x = 0, 5, 10, 15$  and  $20$  at.%) films. The obtained values of  $E_o$ ,  $E_d$  and  $n(0)$  are listed in table 2. It was observed that the single oscillator energy,  $E_o$ , increases while the dispersion energy,  $E_d$ , and the refractive index  $n(0)$  decrease with increasing Ge content.

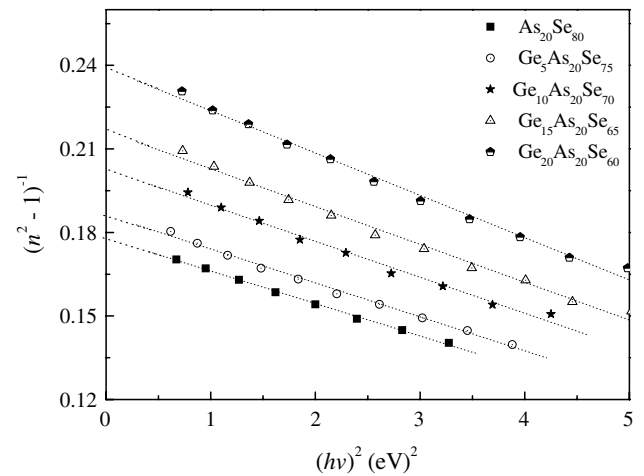
The dependence of the refractive index on the lattice dielectric constant,  $\varepsilon_L$ , is given by [18]:

$$n^2 = \varepsilon_L - (e^2/\pi c^2)(N/m^*)\lambda^2, \quad (6)$$

where  $N/m^*$  is the ratio of the carrier concentration,  $N$ , to the effective mass,  $m^*$ ,  $c$  is the speed of light and  $e$  is the electronic charge. The plots of  $n^2$  versus  $\lambda^2$  for the  $\text{Ge}_x\text{As}_{20}\text{Se}_{80-x}$  (where  $x = 0, 5, 10, 15$  and  $20$  at.%) thin films as shown in figure 4 are linear, verifying equation (6). The values of  $\varepsilon_L$  and  $N/m^*$  were deduced from the extrapolation of these plots to  $\lambda^2 = 0$  and from the slope of the graph, respectively. The obtained values for  $\varepsilon_L$  and  $N/m^*$  for the  $\text{Ge}_x\text{As}_{20}\text{Se}_{80-x}$  (where  $x = 0, 5, 10, 15$  and  $20$  at.%) thin films are listed in table 2.



**Figure 2.** Refractive index dispersion spectra for  $\text{Ge}_x\text{As}_{20}\text{Se}_{80-x}$  (where  $x = 0, 5, 10, 15$  and  $20$  at.%) thin films. Solid curves are determined according to the Cauchy dispersion relationship [15].



**Figure 3.** Plots of refractive index factor  $(n^2 - 1)^{-1}$  versus  $(h\nu)^2$  for  $\text{Ge}_x\text{As}_{20}\text{Se}_{80-x}$  (where  $x = 0, 5, 10, 15$  and  $20$  at.%) thin films.

The decrease in the refractive index,  $n$ , and in the dispersion energy,  $E_d$ , with increasing Ge content could be explained by the decrease in the carrier concentration,  $N$  [19], as shown in table 2.

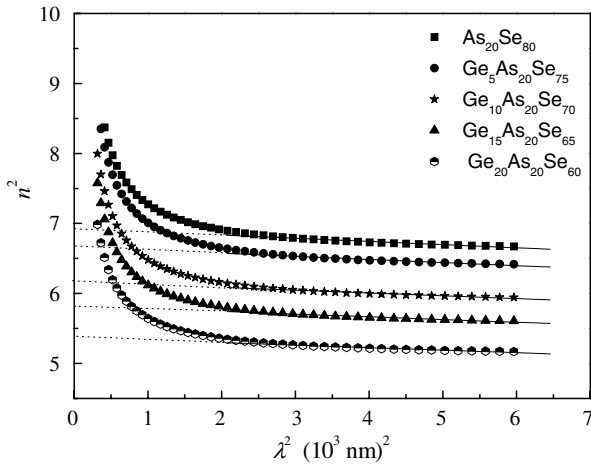
Furthermore, a simple complementary graphical method for deriving the first-order number,  $m_1$ , and film thickness,  $d$ , based on equation (2) was also used. For this purpose equation (2) can now be written for the extremes of the spectrum as [2]

$$\frac{l}{2} = 2d \cdot \left(\frac{n}{\lambda}\right) - m_1, \quad (7)$$

where  $l = 0, 1, 2, 3, \dots$  for the successive tangent points, starting from the long wavelength end, and  $m_1$  is the order number of the first ( $l = 0$ ) tangent point considered. Therefore, by plotting  $(l/2)$  versus  $(n/\lambda)$  we obtain a straight line with the slope  $2d$  and the cut-off on the vertical axis at  $-m_1$  as shown in figure 5. The obtained values of  $2d$  and  $m_1$  for the  $\text{Ge}_x\text{As}_{20}\text{Se}_{80-x}$  (where  $x = 0, 5, 10, 15$  and  $20$  at.%) thin films are displayed as shown in this figure.

**Table 2.** Some physical parameters as a function of Ge content for  $\text{Ge}_x\text{As}_{20}\text{Se}_{80-x}$  (where  $x = 0, 5, 10, 15$  and  $20$  at.%) specimens.

| Composition                                  | $E_g$ (eV) | $E_o$ (eV) | $E_d$ (eV) | $E_o/E_g$ | $n(0)$ | $N/m^*$ ( $10^{43} \text{ m}^3$ ) | $\epsilon_L$ | Excess of Se–Se bonds | CE ( $\text{eV atom}^{-1}$ ) |
|--|------------|------------|------------|-----------|--------|-----------------------------------|--------------|-----------------------|------------------------------|
| $\text{As}_{20}\text{Se}_{80}$               | 1.84       | 3.851      | 21.64      | 2.098     | 2.57   | 5.00                              | 6.93         | 100                   | 2.037                        |
| $\text{Ge}_5\text{As}_{20}\text{Se}_{75}$    | 1.88       | 3.905      | 20.99      | 2.072     | 2.53   | 4.91                              | 6.67         | 70                    | 2.179                        |
| $\text{Ge}_{10}\text{As}_{20}\text{Se}_{70}$ | 1.91       | 3.967      | 19.54      | 2.073     | 2.43   | 4.47                              | 6.17         | 40                    | 2.321                        |
| $\text{Ge}_{15}\text{As}_{20}\text{Se}_{65}$ | 1.97       | 4.010      | 18.59      | 2.042     | 2.37   | 4.28                              | 5.82         | 10                    | 2.463                        |
| $\text{Ge}_{20}\text{As}_{20}\text{Se}_{60}$ | 2.02       | 4.041      | 17.00      | 1.995     | 2.28   | 3.95                              | 5.37         | —                     | 2.53                         |



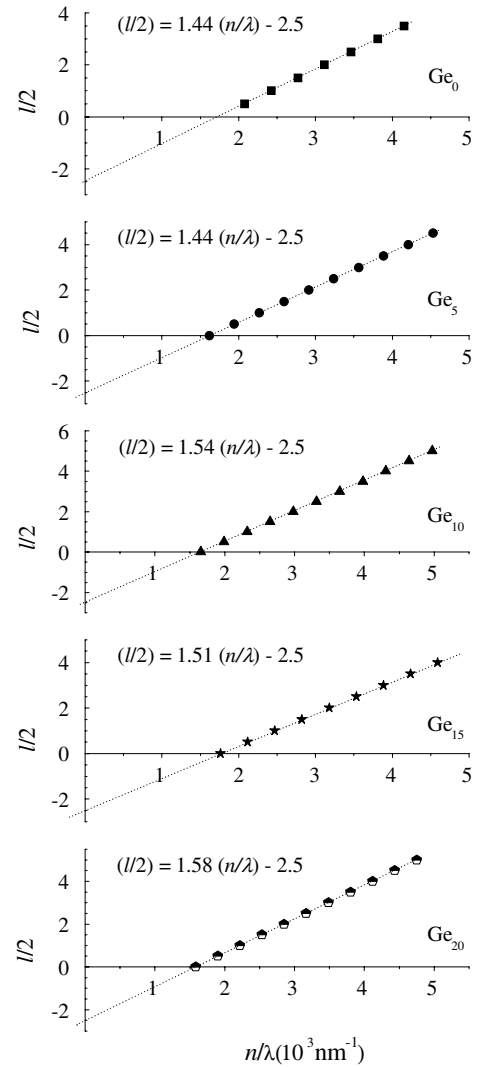
**Figure 4.** Plots of  $n^2$  versus  $\lambda^2$  for  $\text{Ge}_x\text{As}_{20}\text{Se}_{80-x}$  (where  $x = 0, 5, 10, 15$  and  $20$  at.%) thin films.

### 3.2. Determination of the extinction coefficient and optical band gap

Continuing with the description of the data processing method, when there is no substrate in the reference beam and the values of the refractive index and the thickness of the films are already known, the absorption coefficient,  $\alpha$ , is derived using the interference-free transmission spectrum,  $T_\alpha$  (see figure 1), over the whole spectral range, using the well-known equation suggested by Connell and Lewis [20]:

$$\alpha = -\frac{1}{d} \ln \left( \frac{1}{B} \left\{ A + [A^2 + 2BT_\alpha(1 - R_2R_3)]^{1/2} \right\} \right), \quad (8)$$

where  $A = (R_1 - 1)(R_2 - 1)(R_3 - 1)$ ,  $B = 2T_\alpha(R_1R_2 + R_1R_3 - 2R_1R_2R_3)$ ,  $R_1$  is the reflectance of the air–film interface ( $R_1 = [(1 - n)/(1 + n)]^2$ ),  $R_2$  is the reflectance of the film–substrate interface ( $R_2 = [(n - s)/(n + s)]^2$ ) and  $R_3$  is the reflectance of the substrate–air interface ( $R_3 = [(s - l)/(s + 1)]^2$ ). To complete the calculations of the optical constants, the extinction coefficient,  $k$ , is calculated using the values of  $\alpha$  and  $\lambda$  by the well-known relation  $k = \alpha\lambda/4\pi$ . Figure 6 illustrates the dependence of  $k$  on the photon energy for  $\text{Ge}_x\text{As}_{20}\text{Se}_{80-x}$  (where  $x = 0, 5, 10, 15$  and  $20$  at.%) thin films. For  $\alpha \leq 10^5 \text{ cm}^{-1}$ , the imaginary part of the complex index of refraction is much less than  $n$ , so that the previous expressions used to calculate the reflectance are valid. In the region of strong absorption, the interference fringes disappear; in other words, for very large  $\alpha$  the three curves  $T_M$ ,  $T_\alpha$  and  $T_m$  converge to a single curve.

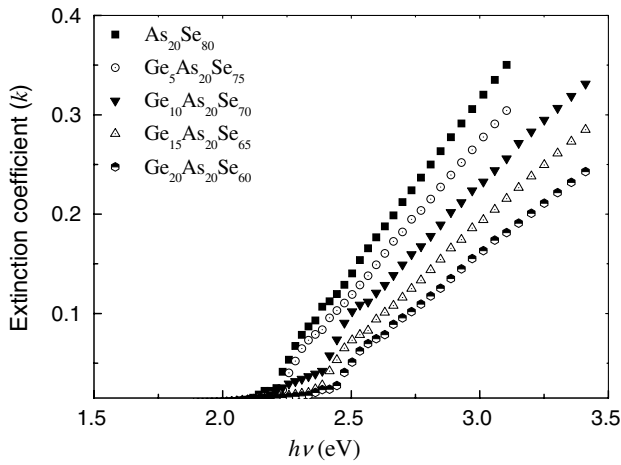


**Figure 5.** Plots of  $(l/2)$  versus  $(n/\lambda)$  to determine the film thickness and the first-order number,  $m_1$ , for  $\text{Ge}_x\text{As}_{20}\text{Se}_{80-x}$  (where  $x = 0, 5, 10, 15$  and  $20$  at.%) thin films.

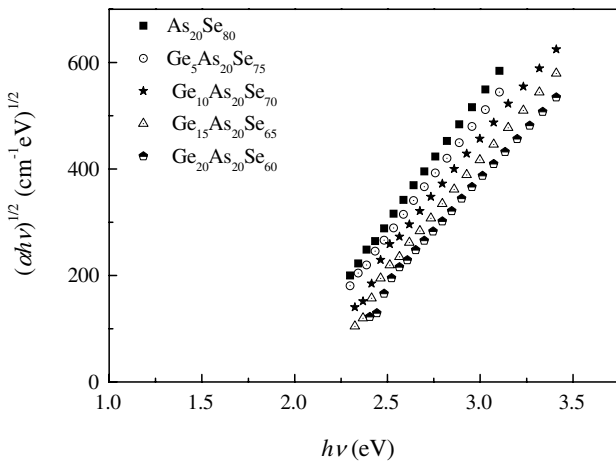
According to Tauc’s relation [21, 22] for allowed non-direct transitions, the photon energy dependence of the absorption coefficient can be described by

$$(\alpha h\nu)^{1/2} = B(h\nu - E_g), \quad (9)$$

where  $B$  is a parameter that depends on the transition probability and  $E_g$  is the optical energy gap. Figure 7 shows the absorption coefficient in the form of  $(\alpha h\nu)^{1/2}$  versus  $h\nu$  for the  $\text{Ge}_x\text{As}_{20}\text{Se}_{80-x}$  (where  $x = 0, 5, 10, 15$  and  $20$  at.%) films.



**Figure 6.** Extinction coefficient,  $k$ , versus  $h\nu$  for  $\text{Ge}_x\text{As}_{20}\text{Se}_{80-x}$  (where  $x = 0, 5, 10, 15$  and  $20$  at.%) thin films.

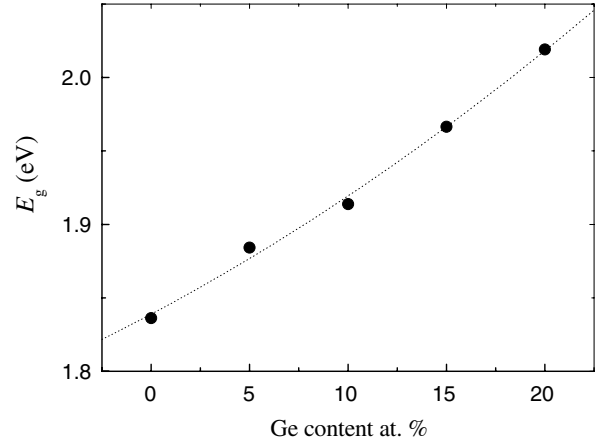


**Figure 7.** Dependence of  $(\alpha h\nu)^{1/2}$  on photon energy,  $h\nu$ , for  $\text{Ge}_x\text{As}_{20}\text{Se}_{80-x}$  (where  $x = 0, 5, 10, 15$  and  $20$  at.%) thin films from which the optical band gap,  $E_g$ , is estimated (Tauc extrapolation).

The intercepts of the straight lines with the photon energy axis yield the values of the optical band gap. The variation of  $E_g$  as a function of the Ge content for the thin films is depicted in figure 8.

From this figure, it is clear that  $E_g$  increases with increasing Ge content for the investigated films. This behaviour is in good agreement with many authors [23–25]. They found that the optical band gap increases with increasing Ge content in the As–Ge–Se and Ge–Se systems. The increase in the optical band gap with increasing Ge content can be interpreted on the basis of the chemical-bond approach proposed by Bicerano and Ovshinsky [26].

Knowing the bond energies of the various bonds involved in the Ge–As–Se system [2], we can estimate the cohesive energy, CE, i.e. the stabilization energy of an infinitely large cluster of the material per atom, by summing the bond energies over all the bonds expected in the system under test. The CE of the prepared samples is evaluated from the following equation  $\text{CE} = \sum (C_i D_i / 100)$ , where  $C_i$  and  $D_i$  are the numbers of the expected chemical bonds and the energy of each corresponding bond, respectively [27]. The calculated



**Figure 8.** Variation in the optical band gap,  $E_g$ , as a function of Ge content for  $\text{Ge}_x\text{As}_{20}\text{Se}_{80-x}$  (where  $x = 0, 5, 10, 15$  and  $20$  at.%) thin films.

values of the CE for all compositions are presented in table 2. It is observed that the CE increases with increasing Ge content. The increase in the CE with increasing Ge content is due to the decrease in the excess of Se–Se homopolar bonds (see table 2). This result is in good agreement with many authors [2, 28, 29].

The bond energies of the bonds involving, namely, Ge–Se, As–Se and Se–Se are, respectively, equal to  $49.44 \text{ kcal mol}^{-1}$ ,  $41.71 \text{ kcal mol}^{-1}$  and  $44.04 \text{ kcal mol}^{-1}$  [2]. For the Ge–As–Se system, Ge and As atoms bond to Se atoms to form  $\text{GeSe}_2$  and  $\text{As}_2\text{Se}_3$  structural units, respectively. After forming Ge–Se and As–Se bonds there are still unsatisfied Se valences which must be satisfied by the formation of Se–Se bonds (Se chains). With increasing Ge content the  $\text{GeSe}_2/\text{Se}$  ratio progressively increases. The optical gap could be obtained from the addition of the partial optical gaps of the different structural phases formed inside the film. With increasing Ge content, the  $\text{GeSe}_2$  ( $E_g = 2.2 \text{ eV}$  [30]) phase replaces the Se ( $E_g = 1.95 \text{ eV}$  [2]) phase which is behind the increase in the optical gap of the films with increasing Ge content.

The increase in the optical band gap, i.e. the increase in the network order, is accompanied by a decrease in polarizability, which leads to the decrease in the refractive index,  $n$ , and in the dispersion energy,  $E_d$ , with increasing Ge content [31].

#### 4. Conclusions

Optical data indicated that the allowed non-direct gap is responsible for the photon absorption in the  $\text{Ge}_x\text{As}_{20}\text{Se}_{80-x}$  thin films. The optical band gap has been determined from the spectral dependence of the absorption coefficient using the Tauc formula. It was found that the optical band gap,  $E_g$ , and the single-oscillator energy,  $E_o$ , increase, while the refractive index,  $n$ , and the dispersion energy,  $E_d$ , decrease with increasing Ge content in the films. The dispersion of the refractive index is discussed in terms of the single-oscillator WDD model. The chemical-bond approach can be applied successfully to interpret the increase in the optical gap with increasing Ge content.

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