

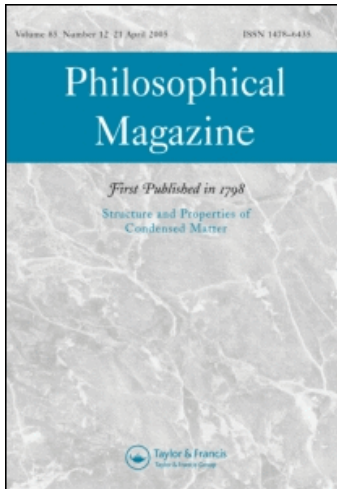
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## Determination of the thickness and optical constants of amorphous Ge–Se–Bi thin films

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The effect of varying bismuth concentration on the optical constants of amorphous  $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$  (where  $x=0, 3, 6, 9$  and  $12$  at%) thin films prepared by thermal evaporation has been investigated. The transmission spectra  $T(\lambda)$  of the films at normal incidence were obtained in the spectral region from  $400$  to  $2500$  nm. An analysis proposed by Swanepoel [J. Phys. E: Sci. Instrum. 16 (1983) p.1214], based on the use of the maxima and minima of the interference fringes, was applied to derive the real and imaginary parts of the complex index of refraction and also the film thickness. Increasing bismuth content was found to affect the refractive index and extinction coefficient of the  $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$  films. Optical absorption measurements show that the fundamental absorption edge is a function of composition. With increasing bismuth content, the refractive index increases while the optical band gap decreases.

**Keywords:** amorphous; thin films; optical transmission

### 1. Introduction

Chalcogenide glasses exhibit unique IR and transmission properties, which make them potentially useful for a wide variety of applications. It was previously believed that the electrical properties of chalcogenides were insensitive to the added impurities, the Fermi level being effectively pinned near the middle of the band gap [1]. The pinning is apparently a consequence of a high density of intrinsic defects in these materials. Generally speaking, chalcogenides are p-type, implying that the Fermi level lies closer to the valence band.

From a view point of device application, obtaining n-type conduction in chalcogenide semiconductors is an important issue. Tohge and co-workers [2,3] and Nagels et al. [4,5] have shown that the addition of Bi atoms to chalcogenide glasses does lead to n-type conduction, while addition of other elements of group V (Sb, As) does not.

Optical properties of thin films have been the subject of intense study over the past decades, and efforts have been made to develop mathematical formulations for describing the transmittance and reflectance of different optical systems [6,7].

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Among the existing methods for determining the optical constants, those based exclusively on the optical transmission spectra at normal incidence have been applied to different crystalline and amorphous materials deposited on transparent substrates in the form of thin films [8–12]. 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  $\sim 1\%$  [10]. They do, however, assume that the film has a uniform thickness, which, when absent, leads to less accurate results and even serious errors.

The aim of the present investigation is to study the effect of Bi atoms on the complex refractive index ( $n_c = n - ik$ ) and other optical constants of amorphous  $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$  (where  $x=0, 3, 6, 9$  and  $12$  at%) thin films. This study was undertaken to obtain a deeper understanding of the physical properties of this interesting chalcogenide system.

## 2. Experimental details

Different compositions of bulk  $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$  (where  $x=0, 3, 6, 9$  and  $12$  at%) chalcogenide glasses were prepared from their high purity components (99.999%) by the melt-quenching technique. The elements were heated together in an evacuated ( $10^{-3}$  Pa) silica ampoule up to 1200 K, and the temperature kept constant for  $\sim 24$  h. During the course of heating, the ampoule was shaken several times to maintain uniformity of the melt. Finally, the ampoule was quenched into ice-cold water to avoid crystallization.

Thin films of  $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$  were prepared by thermal evaporation of the bulk samples. The thermal evaporation process was performed inside a coating system (Edward 306E), at a pressure of approximately  $10^{-3}$  Pa. During the deposition process (at normal incidence), the substrates were rotated to obtain films of uniform thickness.

The elemental compositions of the films were checked using energy-dispersive X-ray (Link Analytical EDX, Witney, UK) spectroscopy. Deviations in the compositions of the evaporated thin films from those in the initial bulk specimens did not exceed 1.0 at%. The amorphous state of the films was checked using an X-ray diffractometer (Philips type 1710 with Cu as target and Ni as filter,  $\lambda = 1.5418$  Å). The absence of crystalline peaks confirmed the amorphous state of the prepared samples.

A double-beam (Jasco V-630) spectrophotometer was used to measure the transmittance of the prepared films in the spectral wavelength range 400–2500 nm. Without a glass substrate in the reference beam, the measured transmittance spectra were used to calculate the optical constants of the films. In the present work, the envelope method suggested by Swanepoel [10] has been applied.

## 3. Results and discussion

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

The optical system under consideration corresponds to homogeneous and uniform thin films, deposited on thick transparent substrates. The thermally evaporated films

have thickness  $d$  and complex refractive index  $n_c = n - ik$ , where  $n$  is the refractive index and  $k$  the extinction coefficient. The thickness of the substrate is several orders of magnitude larger than  $d$ , and its refractive index is symbolized by  $s$ . The substrate is considered to be perfectly smooth, but thick enough so that, in practice, the planes are not perfectly parallel and all interference effects arising from the substrate are destroyed. The system is surrounded by air with refractive index  $n_o = 1$ . Taking all the multiple reflections at the three interfaces into account, it can be shown that, in the case  $k^2 \ll n^2$ , the transmission  $T$  at normal incidence is given by [13–15]

$$T = \frac{Ax}{B - Cx \cos(\phi) + Dx^2}, \tag{1}$$

where  $A = 16n^2s$ ,  $B = (n + 1)^3(n + s^2)$ ,  $C = 2(n^2 - 1)(n^2 - s^2)$ ,  $D = (n - 1)^3(n - s^2)$ ,  $\phi = 4\pi nd/\lambda$  and  $x = \exp(-\alpha d)$ , where  $\alpha$  is the absorption coefficient. The values of the transmission at the maxima and minima of the interference fringes can be obtained from Equation (1) by setting the interference condition  $\cos \phi = +1$  for maxima ( $T_M$ ) and  $\cos \phi = -1$  for minima ( $T_m$ ).

Figure 1 shows the measured transmittance ( $T$ ) spectra, the created envelopes  $T_M$  and  $T_m$ , and the geometric mean,  $T_a = \sqrt{T_M T_m}$  in the spectral region with interference fringes for the  $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$  (where  $x = 0, 6$  and  $12$  at%) thin films, according to Swanepoel’s method based on the idea of Manificier et al. [16]. 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:

$$n_1 = \sqrt{N + \sqrt{N^2 - s^2}}, \tag{2}$$

where

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

Here,  $T_M$  and  $T_m$  are the transmission maxima and the corresponding minima at a certain wavelength  $\lambda$ . Alternatively, one of these values is an experimental interference maximum (minimum) and the other is derived from the corresponding envelope. Both envelopes are computer-generated using the OriginLab (version 7) program. The index of refraction of the substrate  $s$  at each wavelength is derived from  $T_s(\lambda)$ , using the equation [17]:

$$s = \frac{1}{T_s} + \sqrt{\frac{1}{T_s^2} - 1}. \tag{3}$$

The calculated values of the refractive index  $n_1$ , using Equation (2), are listed in Table 1. The accuracy of this initial estimation of the refractive index is improved after calculating  $d$ , as will be explained below. Now, it is necessary to take into account the basic equation for the interference fringes:

$$2nd = m_o \lambda, \tag{4}$$

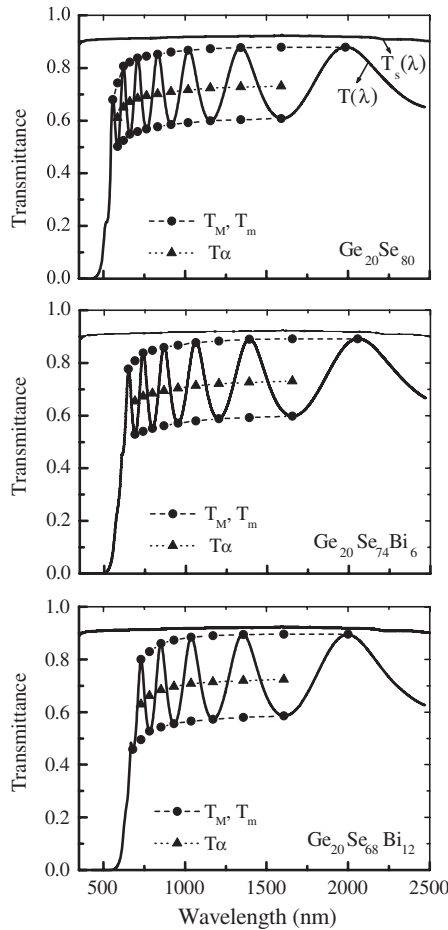


Figure 1. Transmission spectra of  $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$  ( $x=0, 6$  and  $12$  at%) thin films. The average thicknesses of these samples are  $815, 829$  and  $789$  nm for  $x=3, 6$  and  $12$  at%, respectively. Curves  $T_M, T_m$  and  $T_\alpha$ , are according to the text.  $T_s$  is the transmission of the substrate alone.

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

$$d = \frac{\lambda_1 \cdot \lambda_2}{2(n_{c2}\lambda_1 - n_{c1} \cdot \lambda_2)}. \quad (5)$$

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 consequently must 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 (4). 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 extrema point (see Figure 1) and deriving a new thickness  $d_2$ . The values of the

Table 1. Values of  $\lambda$ ,  $T_s$ ,  $T_M$ ,  $T_m$ ,  $n_1$ ,  $d_1$ ,  $m_o$ ,  $d_2$  and  $n_2$  for  $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$  ( $x=0, 6$  and  $12$  at%) thin films from transmission spectra of Figure 1. The underlined values of transmittance are those given in the transmittance spectra of Figure 1; the others are calculated by the envelope method.

Composition	$\lambda$	$T_s$	$T_M$	$T_m$	$n_1$	$d_1$	$m_o$	$m$	$d_2$	$n_2$	
$\text{Ge}_{20}\text{Se}_{80}$	1591	0.918	0.878	<u>0.608</u>	2.426		2.49	2.5	816	2.429	
	1341	0.918	<u>0.877</u>	<u>0.604</u>	2.459		2.99	3.0	815	2.461	
	1156	0.918	<u>0.873</u>	<u>0.600</u>	2.475	815	3.48	3.5	816	2.478	
	1020	0.918	<u>0.868</u>	<u>0.592</u>	2.505	799	4.00	4.0	811	2.493	
	915	0.918	<u>0.860</u>	<u>0.585</u>	2.525	805	4.49	4.5	813	2.521	
	833	0.916	<u>0.852</u>	<u>0.577</u>	2.546	835	4.98	5.0	816	2.549	
	764	0.914	<u>0.845</u>	<u>0.569</u>	2.569	826	5.47	5.5	816	2.571	
	709	0.914	<u>0.838</u>	<u>0.558</u>	2.600	814	5.97	6.0	816	2.602	
	661	0.912	<u>0.822</u>	<u>0.548</u>	2.621	826	6.46	6.5	817	2.628	
	622	0.912	<u>0.807</u>	<u>0.525</u>	2.691	754	7.05	7.0	806	2.663	
	586	0.912	<u>0.744</u>	<u>0.502</u>	2.674	–	7.44	7.5	819	2.687	
	$\bar{d}_1 = 812, \delta_1 = 24 \text{ nm (3\%)}; \bar{d}_2 = 815, \delta_2 = 3.4 \text{ nm (0.42\%)}$										
	$\text{Ge}_{20}\text{Se}_{74}\text{Bi}_6$	1654	0.918	0.891	<u>0.598</u>	2.483		2.48	2.5	833	2.494
1390		0.918	<u>0.890</u>	<u>0.593</u>	2.521		3.00	3.0	827	2.515	
1204		0.918	<u>0.883</u>	<u>0.588</u>	2.536	826	3.48	3.5	831	2.542	
1061		0.918	<u>0.877</u>	<u>0.580</u>	2.565	828	4.00	4.0	827	2.560	
952		0.918	<u>0.868</u>	<u>0.571</u>	2.592	811	4.50	4.5	826	2.584	
867		0.916	<u>0.859</u>	<u>0.561</u>	2.621	826	4.99	5.0	827	2.615	
796		0.914	<u>0.848</u>	<u>0.551</u>	2.646	832	5.5	5.5	827	2.641	
739		0.914	<u>0.838</u>	<u>0.540</u>	2.674	839	5.99	6.0	829	2.674	
690		0.912	<u>0.808</u>	<u>0.529</u>	2.676	–	6.41	6.5	838	2.705	
$\bar{d}_1 = 827, \delta_1 = 9.2 \text{ nm (1.1\%)}; \bar{d}_2 = 829, \delta_2 = 3.8 \text{ nm (0.46\%)}$											
$\text{Ge}_{20}\text{Se}_{68}\text{Bi}_{12}$	1607	0.918	0.895	<u>0.586</u>	2.533		2.50	2.5	793	2.546	
	1358	0.918	<u>0.894</u>	<u>0.579</u>	2.578		3.01	3.0	790	2.582	
	1172	0.918	<u>0.890</u>	<u>0.573</u>	2.603	775	3.52	3.5	788	2.599	
	1038	0.918	<u>0.884</u>	<u>0.566</u>	2.629	789	4.02	4.0	790	2.631	
	933	0.916	<u>0.873</u>	<u>0.556</u>	2.659	795	4.52	4.5	789	2.661	
	853	0.914	<u>0.860</u>	<u>0.543</u>	2.694	799	5.01	5.0	791	2.703	
	782	0.914	<u>0.830</u>	<u>0.528</u>	2.711	810	5.50	5.5	793	2.726	
	730	0.914	<u>0.800</u>	<u>0.495</u>	2.806	–	6.10	6.0	780	2.776	
$\bar{d}_1 = 793, \delta_1 = 13 \text{ nm (1.6\%)}; \bar{d}_2 = 789, \delta_2 = 4 \text{ nm (0.5\%)}$											

thickness in this way have a smaller dispersion. It should be emphasized that the accuracy of the final thickness is better than 1% (Table 1).

With the accurate values of  $m_o$  and the average value  $\bar{d}_2$  of  $d_2$ , expression (4) 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 wavelength for different compositions of the amorphous  $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$  (where  $x=0, 6$  and  $12$  at%) thin films. The relative error in  $n$ ,  $\Delta n/n$ , does not exceed the precision of the measurements  $\Delta T/T$  ( $\pm 1\%$ ). Now, the values of  $n_2$  can be fitted to a function such as the two-term Cauchy dispersion relationship [18]:

$$n(\lambda) = a + \frac{b}{\lambda^2}, \tag{6}$$

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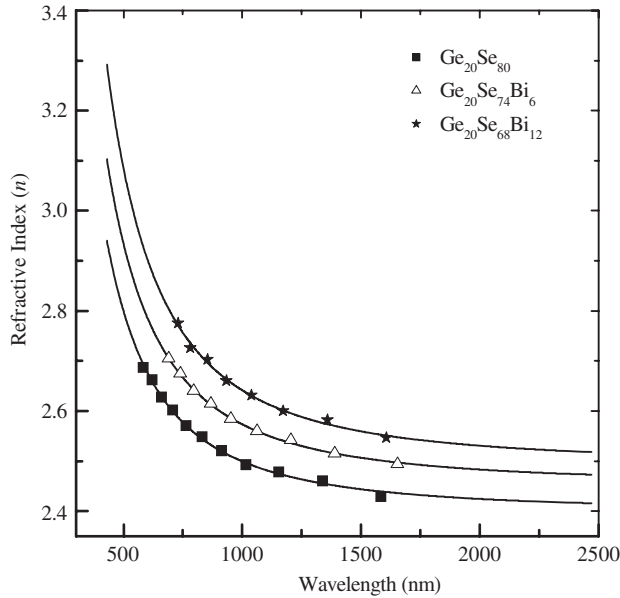


Figure 2. Refractive index dispersion spectra for  $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$  ( $x=0, 6$  and  $12$  at%) thin films. Solid curves are determined according to the Cauchy dispersion relationship [18].

which can then be used to extrapolate the wavelength dependence beyond the range of measurement (Figure 2). The least-squares fit of  $n_2$  for the different samples listed in Table 1 yields  $n = 2.4 + (1.00 \times 10^5/\lambda^2)$  for  $\text{Ge}_{20}\text{Se}_{80}$ ,  $n = 2.45 + (1.2 \times 10^5/\lambda^2)$  for  $\text{Ge}_{20}\text{Se}_{74}\text{Bi}_6$  and  $n = 2.49 + (1.48 \times 10^5/\lambda^2)$  for  $\text{Ge}_{20}\text{Se}_{68}\text{Bi}_{12}$  thin films.

The final values of the refractive index can be fitted to an appropriate function such as the Wemple–DiDomenico (WDD) dispersion relationship [19], i.e. to the single-oscillator model:

$$n^2(h\nu) = 1 + \frac{E_o E_d}{E_o^2 - (h\nu)^2}, \quad (7)$$

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  $E_g$ :  $E_o \approx 2E_g$ , as was found by Tanaka [20]. Figure 3 also shows the values of the refractive index  $n(0)$  at  $h\nu=0$  for the  $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$  ( $x=0, 3, 6, 9$  and  $12$  at%) films. The obtained values of  $E_o$ ,  $E_d$  and  $n(0)$  are listed in Table 2. It can be observed that the single oscillator energy  $E_o$  and the dispersion energy  $E_d$  decrease with the increase in Bi content, while the refractive index  $n(0)$  increases. An important achievement of the WDD model is that it relates the dispersion energy  $E_d$  to other physical parameters of the material through the following empirical relationship [19]:

$$E_d = \beta N_c Z_a N_e \text{ (eV)}, \quad (8)$$

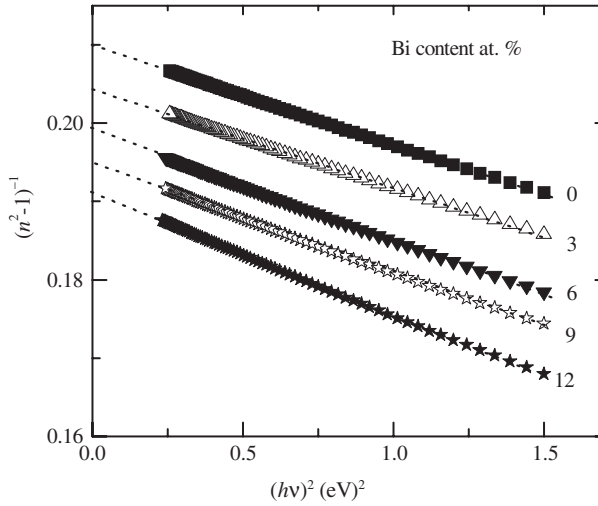


Figure 3. Plots of refractive index factor  $(n^2 - 1)^{-1}$  versus  $(hv)^2$  for  $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$  ( $x=0, 3, 6, 9$  and  $12$  at%) thin films.

Table 2. Wemple–DiDomenico dispersion parameters ( $E_o$  and  $E_d$ ), values of the refractive index  $n(0)$  extrapolated to  $h\nu=0$ , lattice dielectric constant  $\epsilon_L$ ,  $N/m^*$  ratio and the excess of Se–Se bonds for  $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$  ( $x=0, 3, 6, 9$  and  $12$  at%) thin films.

Composition	$E_o$ (eV)	$E_d$ (eV)	$n(0)$	$\epsilon_L$	$N/m^*$ ( $10^{31}/\text{cm}^3$ )	Excess of Se–Se bonds
$\text{Ge}_{20}\text{Se}_{80}$	4.07	19.38	2.40	5.96	2.48	40
$\text{Ge}_{20}\text{Se}_{77}\text{Bi}_3$	3.93	19.22	2.43	6.11	2.78	33
$\text{Ge}_{20}\text{Se}_{74}\text{Bi}_6$	3.79	19.06	2.45	6.26	2.99	25
$\text{Ge}_{20}\text{Se}_{71}\text{Bi}_9$	3.64	18.65	2.48	6.39	3.36	18
$\text{Ge}_{20}\text{Se}_{68}\text{Bi}_{12}$	3.49	18.24	2.50	6.52	3.72	10

where  $N_c$  is the effective coordination number of the cation nearest-neighbor to the anion,  $Z_a$  is the formal chemical valency of the anion,  $N_e$  is the effective number of valence electrons per anion and  $\beta = 0.37 \pm 0.04$  eV for covalent crystalline and amorphous materials. Therefore, to account for the compositional trended of  $E_d$ , it is suggested that the observed decrease in  $E_d$  with increasing Bi content is primarily due to the change in the ionicities, which increase with Bi content.

The dependence of the refractive index ( $n$ ) on the lattice dielectric constant  $\epsilon_L$  is given by [21]

$$n^2 = \epsilon_L - (e^2/\pi c^2)(N/m^*)\lambda^2, \tag{9}$$

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  $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$  (where  $x=0, 3, 6, 9$  and  $12$  at%) thin films as shown in Figure 4 are linear, verifying Equation (9). The values of  $\epsilon_L$  and  $N/m^*$  were deduced from the extrapolation of these plots to  $\lambda^2=0$  and from the slope of the graph, respectively.



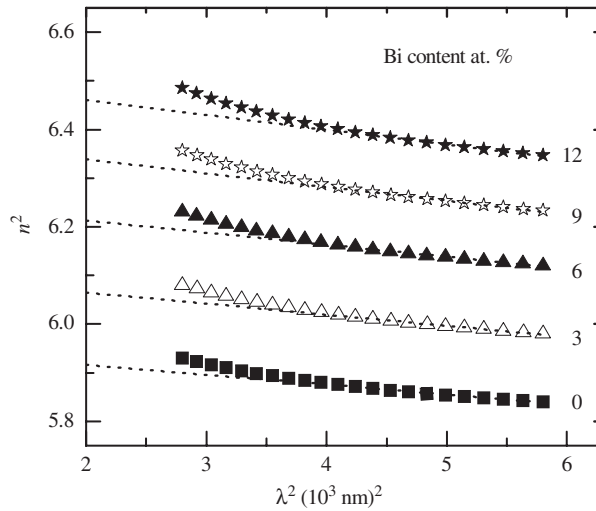


Figure 4. Plots of  $n^2$  versus  $\lambda^2$  for  $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$  ( $x=0, 3, 6, 9$  and  $12$  at%) thin films.

The obtained values for  $\epsilon_L$  and  $N/m^*$  for the  $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$  films are listed in Table 2. Furthermore, a simple complementary graphical method for deriving the first-order number  $m_1$  and film thickness  $d$ , based on Equation (4), was also used. For this purpose Equation (4) can now be written for the extrema of the spectrum as

$$\frac{l}{2} = 2d\left(\frac{n}{\lambda}\right) - m_1, \tag{10}$$

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, where  $m_1$  is an integer or a half-integer for the upper or lower tangent points, respectively. Therefore, by plotting  $(l/2)$  versus  $(n/\lambda)$ , we obtain a straight line with slope  $2d$  and cut-off on the vertical axis at  $-m_1$  as shown in Figure 5. The obtained values of  $2d$  and  $m_1$  for the  $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$  films are displayed in Figure 5.

### 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  $n$  and the thickness  $d$  of the films are already known, the absorption coefficient  $\alpha$  is derived via the interference-free transmission spectrum  $T_\alpha$  (see Figure 1) over the whole spectral range, using the equation suggested by Connell and Lewis [22]:

$$\alpha = -\frac{1}{d} \ln\left(\frac{1}{B} \{A + [A^2 + 2BT_\alpha(1 - R_2R_3)]^{1/2}\}\right), \tag{11}$$

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

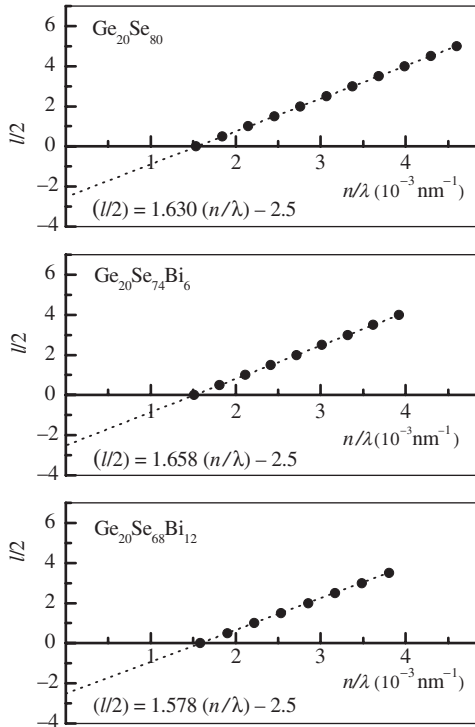


Figure 5. Plots of  $(l/2)$  versus  $(n/\lambda)$  to determine the film thickness and the first-order number  $m_1$  for  $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$  ( $x = 0, 6$  and  $12$  at%) thin films.

of film–substrate interface ( $R_2 = [(n - s)/(n + s)]^2$ ) and  $R_3$  is the reflectance of the substrate–air interface ( $R_3 = [(s - 1)/(s + 1)]^2$ ). To complete the calculations of the optical constants, the extinction coefficient  $k$  is calculated using the values of  $\alpha$  and  $\lambda$  by the relation

$$k = \alpha\lambda/4\pi. \tag{12}$$

Figure 6 illustrates the dependence of  $k$  on wavelength for  $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$  films. For  $\alpha \leq 10^5 \text{ cm}^{-1}$ , the imaginary part of the complex index of refraction is much less than  $n$ , so 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.

According to Tauc’s relation [23, 24] for amorphous semiconductors, the photon energy dependence of the absorption coefficient can be described by

$$(\alpha h\nu)^{1/2} = B(h\nu - E_g), \tag{13}$$

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  $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$  films. 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

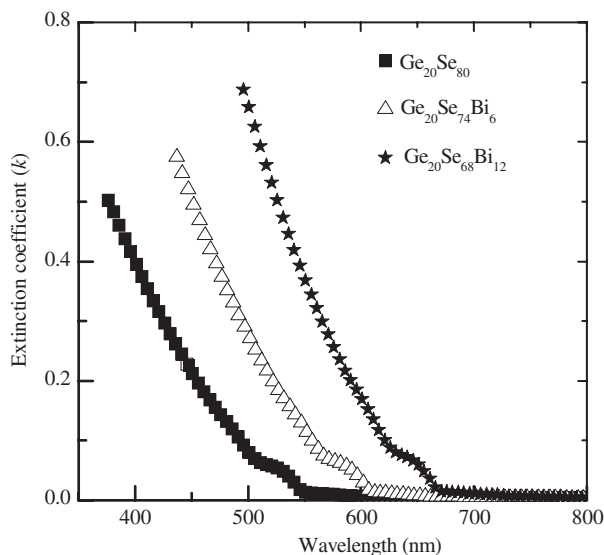


Figure 6. Extinction coefficient  $k$  versus  $\lambda$  for  $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$  ( $x=0, 6$  and  $12$  at%) thin films.

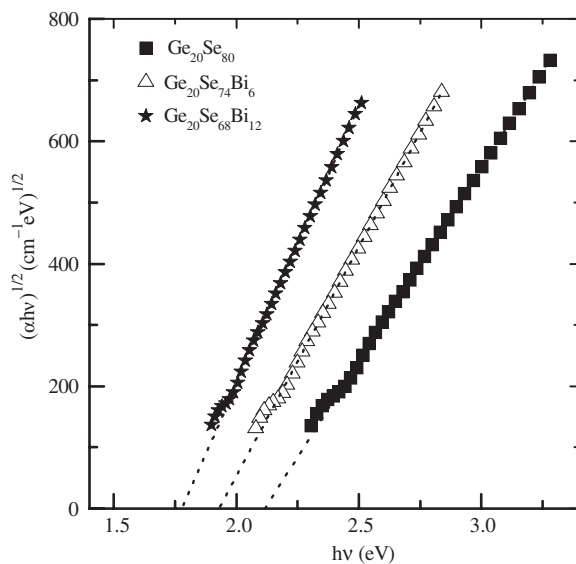


Figure 7. Dependence of  $(\alpha hv)^{1/2}$  on photon energy ( $hv$ ) for  $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$  ( $x=0, 6$  and  $12$  at%) thin films from which the optical band gap  $E_g$  is estimated by a Tauc extrapolation.

a function of Bi content for the films is depicted in Figure 8. From this figure, it is clear that  $E_g$  decreases with increasing Bi content for the investigated films. The decrease in the optical band gap with increasing Bi content can be interpreted on the basis of the chemical-bond approach proposed by Bicerano and Ovshinsky [25]. The chemical-bond approach assumes that: (a) atoms combine more favorably with atoms of different types than with the same type. Bonds between like atoms will

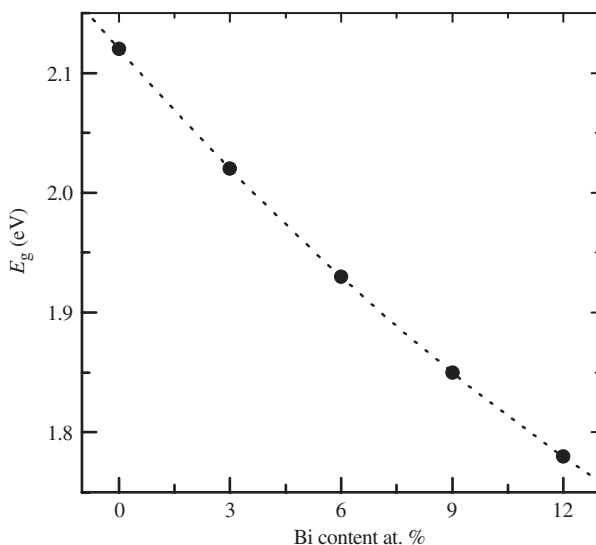


Figure 8. Variation in the optical band gap  $E_g$  as a function of Bi content for  $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$  ( $x = 0, 3, 6, 9$  and  $12$  at%) thin films.

then only occur if there is an excess of a certain type of atom; (b) bonds are formed in the sequence of decreasing bond energy until all the available valencies of the atoms are saturated; (c) each constituent atom is coordinated by  $8-N$  atoms, where  $N$  is the number of outer shell electrons. The presence of any dangling bonds and the other valence defects is neglected.

The bond energies of the various bonds involved, namely, Ge–Se, Bi–Se and Se–Se are, respectively, equal to 49.44, 40.7 and 44.04 kcal/mol [26, 27]. For the first composition ( $\text{Ge}_{20}\text{Se}_{80}$ ), since the Ge–Se bond has the largest bond energy, it is expected that Se atoms would first completely saturate the valences of Ge atoms to form  $\text{GeSe}_2$  structural units. After forming Ge–Se bonds, there are still unsatisfied Se valences which must be satisfied by the formation of Se–Se bonds (Se chains). The number of excess Se–Se bonds for the  $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$  system is given in Table 2. As Bi replaces Se in the  $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$  system, Bi atoms bond to Se atoms to form  $\text{Bi}_2\text{Se}_3$  structural units. With increasing Bi content, the number of Bi–Se bonds increases at the expense of Se–Se bonds, i.e. the  $\text{Bi}_2\text{Se}_3/\text{Se}$  ratio progressively increases and some of the original Se phase is replaced by  $\text{Bi}_2\text{Se}_3$  structural units. The optical gap could be obtained from addition of the partial optical gaps of the different structural phases formed inside the film. With increasing Bi content, the  $\text{Bi}_2\text{Se}_3$  ( $E_g = 0.67$  eV [28]) phase replaces the Se ( $E_g = 1.95$  eV [26]) phase, which accounts for the reduction of the optical gap.

#### 4. Conclusions

The optical band gaps of  $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$  (where  $x = 0, 3, 6, 9$  and  $12$  at%) thin films have been determined from the spectral dependence of the absorption coefficient

using the Tauc formula. It was found that the optical band gap  $E_g$ , the single oscillator energy  $E_o$  and the dispersion energy  $E_d$  decrease, while the refractive index increases with increasing the Bi content in the films. The dispersion of the refractive index is discussed in terms of the single-oscillator Wemple–DiDomenico model. The chemical bond approach can be applied successfully to interpret the decrease in the optical gap with increasing Bi content.

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