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Spectral dependence of the complex refractive index of GeS_2 chalcogenide glass thin films

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The excellent transmittance of chalcogenide glassy semiconductors [1], reaching up to the far-infrared spectra region, and the wide range of photo-induced effects that they exhibit [2], generally accompanied by significant changes in their optical constants, make it possible to use them as absorption filters and many other optical elements [3]. Knowledge of the optical properties of these amorphous materials is obviously necessary for exploiting their very interesting technological potential. This letter is concerned with the optical characterization of as-deposited GeS_2 chalcogenide glass films, prepared by vacuum thermal evaporation, using a very accurate data-processing method proposed by Swanepoel [4], based only on their optical transmission spectra [5, 6].

Thin-film samples were deposited by vacuum evaporation of powdered glassy material (prepared by heating appropriate mixtures of the elements in vacuum-sealed fused-silica ampoules, for about 4 h at 900 8C, and then air-quenching) onto room-temperature glass substrates (BDH microscope slides). The thermal evaporation process was carried out in a coating system (Edwards, model E306A) at a pressure of $\sim 10^{-4}$ Pa from a suitable quartz crucible. The substrates were conveniently rotated at a speed of ~45 r.p.m. during the deposition process, by means of a rotary workholder, which makes it possible to obtain thin films of remarkably uniform thickness [7]. The average deposition rate was $\sim 0.4\ \mathrm{nm\,s^{-1}}$, and the rate was continuously measured by a quartz-crystal monitor (Edwards, model FTM-5). Such a low deposition rate produces a film composition very close to that of the bulk starting material (energy dispersive X-ray analysis (EDAX) measurements have indicated that the film stoichiometry is correct to ±1 at %). The lack of crystallinity in the thin films was verified by X-ray diffraction (XRD) analysis; the XRD pattern is shown in Fig. 1. The thickness of the a-GeS_2 films studied ranged between around 600 and 1200 nm. The optical transmission spectra at normal incidence, used for calculating the optical constants, were obtained by a double-beam ratio recording ultraviolet/visible/near infrared (UV/VIS/NIR) computer-controlled spectrophotometer (Perkin-Elmer, model Lambda-19).

The optical system under consideration corresponds to homogeneous and uniform thin films, deposited on thick, transparent substrates. The thermally-evaporated films had thickness d and complex refractive index $n_c = n - ik$, where n is the refractive index and k the extinction coefficient, which can be expressed in terms of the absorption coefficient Æ, by the equation $k = Æ°/4ð$; the thickness of the substrates was several orders of magnitude greater than d, and their refractive index is symbolized by s. Interference effects gave rise to oscillating curves like that in Fig. 1: such interference fringes were used to accurately determine the optical constants of the chalcogenide films under study.

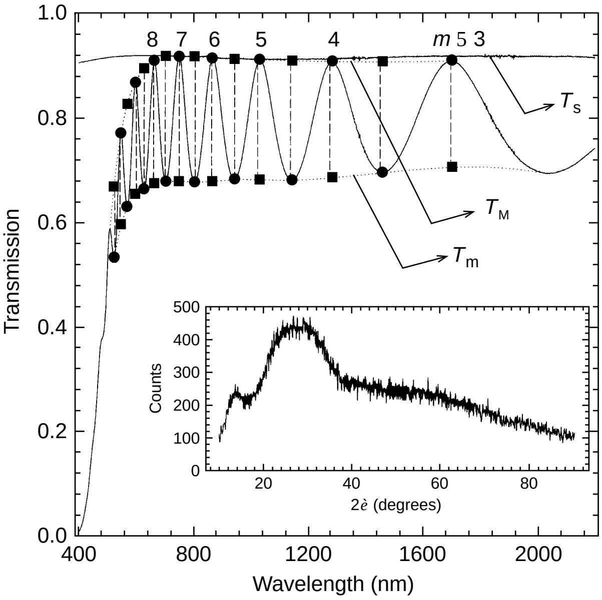

Figure 1 Experimental optical transmission spectrum corresponding to an a-GeS_2 thin film; curves T_M and T_m are the maximum and minimum envelopes, respectively, and T_s is the transmission of the substrate alone. The inset shows the XRD pattern (Cu$K_Æ$ radiation) corresponding to this particular film.

Optical transmission $T(°;\ s,\ n,\ d,\ k)$ is a very complex function, which can be simplified by neglecting the extinction coefficient k, an approximation that is certainly valid over most of the spectrum (Fig. 1 clearly shows that a-GeS_2 films are reasonably transparent over a very wide range of the spectrum), so that, with $k = 0$, the expression for T then becomes

$$T(°;\ s,\ n,\ d,\ k) = \frac{Ax}{B - Cx\cos ö + Dx^2} \qquad (1)$$

where $A = 16n^2 s$, $B = (n+1)^3(n+s^2)$, $C =$

$2(n^2 - 1)(n^2 - s^2)$, $D = (n - 1)^3(n - s^2)$, $ö = 4ðnd/°$ and x, the absorbance, is given by $x = \exp(-Æd)$. In addition, the values of the transmission at the extrema of the interference fringes can be obtained from Equation 1 by setting the interference conditions $\cos ö = 1$ and $\cos ö = -1$ for maxima, T_M, and minima, T_m, respectively.

On the other hand, according to Swanepoel's method, which is based on the idea of Manifacier *et al.* [8] of creating the envelopes of the interference maxima and minima (see Fig. 1), a first, approximate value of the refractive index of the film, n_1, in the spectral region of medium and weak absorption, can be derived by the expression:

$$n_1 = [N + (N^2 - s^2)]^{1/2} \tag{2}$$

where

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

Moreover, the s value at each $°$ was obtained by independently measuring the transmittance of the substrate alone, T_s [4]. The n_1 values are calculated from Equation 2, and the accuracy of the initial computation of the refractive index is notably improved after calculating d, taking into account the well-known, basic equation for the interference fringes, $2nd = m°$, where the order number m is an integer for maxima and half-integer for minima. The first, approximate value of d is given by

$$d_1 = \frac{°_1 °_2}{2(n_{e2}°_1 - n_{e1}°_2)} \tag{3}$$

where n_{e1} and n_{e2} are the refractive indices at two adjacent maxima (or minima) at $°_1$ and $°_2$. The average value of d_1 is now used, along with n_1, to calculate an "order number" m_0 for the different extrema, using the equation for the interference fringes. The accuracy of d is now significantly increased by taking the exact integer or half-integer values of m corresponding to each extreme, and deriving a new thickness, d_2, from the expression for the interference fringes, again using the n_1 values. With the $\bar{d}_2$ value, the final values of the refractive index, n_2, are obtained (see Fig. 2). The block diagram of the algorithm for deriving the thickness and the spectral dependence of the refractive index of a thin layer is given in Fig. 3. In the representative a-GeS$_2$ film under analysis the $\bar{d}_2$ value was found to be 1161 ± 19 nm (1.6%), in complete agreement with the value of the film thickness obtained using an alternative optical method proposed by Minkov [9, 10]. In addition, the film thickness determined by mechanical measurements, using a surface profiling stylus (Sloan, Dektak 3030), on the same film area, was 1148 ± 22 nm, in excellent agreement with the thickness calculated by the optical method (the difference is less than 2%).

Next, the values of n_2 are fitted to the Wemple–DiDomenico dispersion relationship [11, 12]:

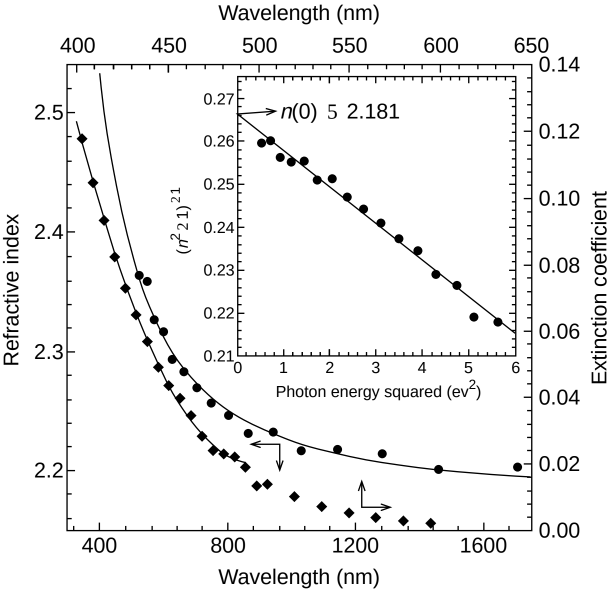

Figure 2 Refractive index and extinction coefficient plotted against wavelength. The inset is a plot of the refractive index factor $(n^2 - 1)^{-1}$ against $("ø)^2$ (the $n(0)$ value is the refractive index extrapolated to $"ø = 0$).

$$n^2(ø) = 1 + \frac{E_0 E_d}{E_0{}^2 - ("ø)^2} \tag{4}$$

where E_0 is the single-oscillator energy and E_d the dispersion energy. By plotting $(n^2 - 1)^{-1}$ against $("ø)^2$ and fitting a straight line, as shown in Fig. 2, E_0 and E_d are determined from the gradient, $(E_0 E_d)^{-1}$, and intercept, E_0/E_d, on the vertical axis; the values of the dispersion parameters E_0 and E_d obtained are 5.60 and 21.03 eV, respectively. The dispersion energy or oscillator strength E_d follows a simple empirical relationship, $E_d = âN_c Z_a N_e$, where â is a constant, and, according to Wemple [12], for covalent crystalline and amorphous materials has a value of 0.37 ± 0.04 eV. N_c is the number of nearest neighbour cations to the anion, Z_a is the formal chemical valency of the anion and N_e is the effective number of valence electrons per anion. In the present case, $N_e = 8$ and $Z_a = 2$, therefore N_c is ~ 3.6.

Since the values of the refractive index are already known over the spectral region studied, from the above-mentioned optical discussion relationship, the absorbance is now calculated using the formulae suggested by Swanepoel. In the region of medium and weak absorption the x values are determined from:

$$x(°) = \frac{E_M - [E_M{}^2 - (n^2 - 1)^3(n^2 - s^4)]^{1/2}}{(n - 1)^3(n - s^2)} \tag{5}$$

where

$$E_M = \frac{8n^2 s}{T_M} + (n^2 - 1)(n^2 - s^2)$$

In the region of strong absorption the interference fringes disappear. If interference effects are ignored, Equation 1 can be written for $x \ll 1$ as $T_0 = Ax/B$ or:

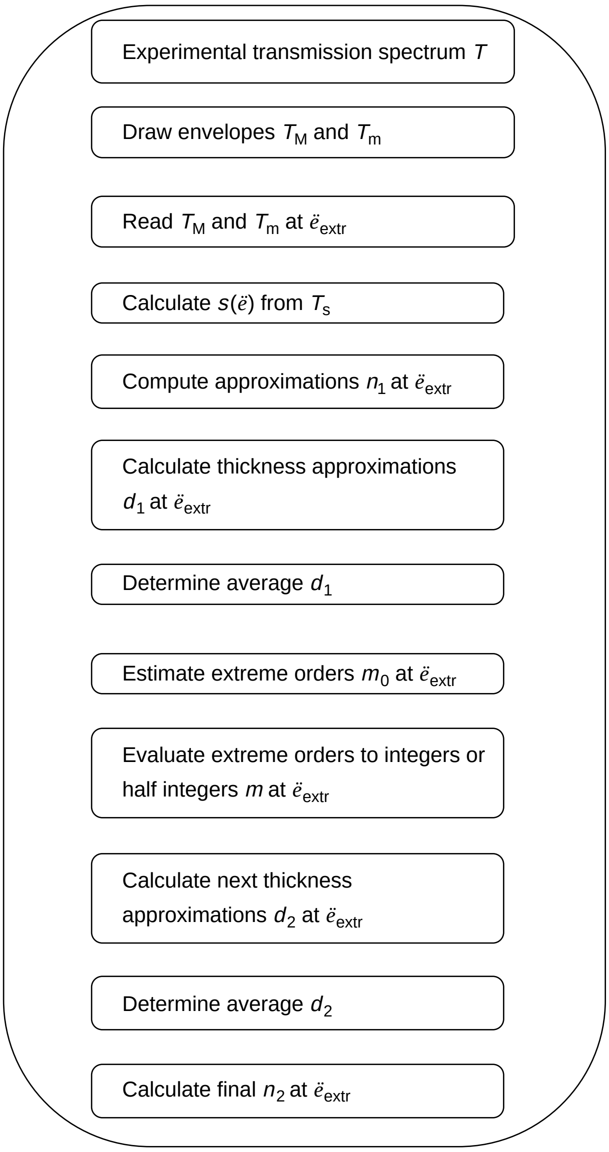

Figure 3 Block diagram of the algorithm of the method for calculating the thickness and the spectral dependence of the refractive index of a thin layer from the optical transmission spectrum only. The symbols are defined in the text.

$$x(°) \approx \frac{(n+1)^2(n+s^2)}{16n^2 s} T_0 \qquad (6)$$

The optical absorption coefficient spectrum derived by Equations 5 and 6 for the representative a-GeS_2 film is depicted in Fig. 4. In the high-absorption spectral region ($Æ$. $\sim 10^4$ cm^{-1}) the $Æ$ values are fitted to the Tauc law (this part of the absorption edge is described on the basis of the "non-direct transition" model proposed by Tauc [13–15]):

$$Æ = \frac{B("ø - E_g{}^{opt})^2}{"ø} \qquad (7)$$

where $E_g{}^{opt}$ is the Tauc bandgap and B is an energy-independent constant; the value of $E_g{}^{opt}$ is obtained by extrapolating $(Æ"ø)^{1/2}$ towards zero (see Fig. 4). For the chalcogenide glassy composition GeS_2, the value of $E_g{}^{opt}$ was found to be 2.33 eV and agrees completely with that reported by Spence and Elliott [16] (the ratio $E_0/E_g{}^{opt}$ takes the value 2.40).

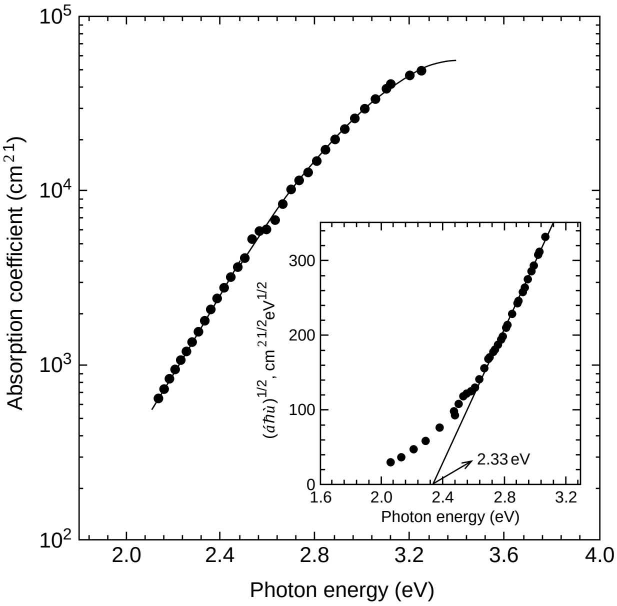

Figure 4 Optical-absorption edge for the glass composition GeS_2 and, in the inset, the associated Tauc extrapolation.

Continuing with the analysis of the optical absorption edge, at lower $Æ$ values (the intermediate absorption range, 1 cm^{-1} , $\sim Æ$, $\sim 10^4$ cm^{-1}), the absorption coefficient depends exponentially upon photon energy, according to the Urbach rule [13–15]: $Æ = Æ_0 \exp("ø/E_1)$, where E_1 is a slope parameter (see Fig. 4); the value of E_1 for the present stoichiometric composition is $\sim$ 190 meV.

In order to complete the computation of the optical constants, the extinction coefficient is determined from the $Æ$ values, using the above-mentioned formula, $k = Æ°/4ð$. Fig. 2 also illustrates the dependence of k upon wavelength. It must be emphasized that the excellent accuracy of the results obtained, in the derivation of the spectral dependence of the complex refractive index, has been confirmed by comparing the experimental transmission spectrum, shown in Fig. 1, with the simulated transmission spectrum, obtained by substituting the calculated thickness and optical constants in the exact expression for the optical transmission at normal incidence [14]. To summarize, the appealing procedure suggested by Swanepoel for using only the transmission spectrum to calculate d and $n_c(°)$ has proved to be very useful in the case of GeS_2 semiconducting glass films as long as they have a reasonably uniform thickness.

Finally, it should be pointed out that several as-deposited a-GeS_2 thin films were illuminated by an Hg arc lamp (through an IR-cut filter and using an intensity of $\sim$ 30 mW cm^{-2}), and the effect of the illumination was a strong blueshift of their transmission spectra, i.e. a clear photo-bleaching process had taken place in these particular chalcogenide samples [16–19].

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