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Computer program PARAV for calculating optical constants of thin films and bulk materials: Case study of amorphous semiconductors

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A computer program **"PARAV"** for calculating various optical constants, e.g., the dispersion of refractive index, optical absorption coefficient, optical thickness and optical bandgap, from experimentally measured transmission spectra of bulk materials and thin films is developed. User-friendly interface, convenient input and output of the measured and calculated data in the form of text files are also a feature of this software. Data from amorphous semiconductors (chalcogenide glasses and thin films and a-Si:H) are used as typical examples to check the reliability of the program.

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1. Introduction

High sensitivity of the optical absorption edge of chalcogenide glasses (ChG) to external factors, such as photo-illumination [1,2], irradiation with high-energy particles and γ-rays [3], pressure [4], etc. is a major research interest over the past few years for their fundamental understanding and also for device applications. The simplest way to record the effect in the fundamental optical absorption edge region is to measure transmission characteristics. In turn, transmission spectra usually are used to determine absorption coefficient, optical bandgap, thickness of thin films, etc. [5]. Such calculations demand a significant data processing, managing of different files and formats. As a rule, the universal computer software are normally used for these purposes, such as Mathematics, Maple, Mathcad and others, which are tedious and require expensive licences and knowledge of the software. However, the script creating process, programming and then managing of files, if, for example, there are many files with input data and from different spectrophotometers takes a lot of time of the researchers. There are some commercially available programs for extracting parameters from the optical transmission data, such as TFCalc (Scientific Software, Inc.), "Refractor" [6] and others, but they are expensive and/or difficult to obtain. So, creating of the computer program with user friendly interface to calculate simplest things, such as absorption coefficient, Tauc plot, optical gap, thin film thickness and refractive index using transmission spectra only is the need for various researchers in many areas of research, especially those studying thin films.

In the present paper, we present to the scientific community an user friendly program **"PARAV"** which calculates very easily the optical constants from transmission spectra of bulk and thin films. To confirm the reliability and the validity of the program, we use the transmission data for a-chalcogenides (thin films and bulk) and a-Si:H and estimate various optical constants, e.g., refractive index (n) as a function of wavelength (λ), thickness (d), optical absorption coefficient (α) and optical bandgap (E_g). We anticipate that Parav can be used not only for amorphous semiconductos, but also for transmission spectra of other materials recorded in the fundamental absorption edge region.

2. Interface

The program consists of two sub programs. The first sub program is used to calculate optical constants from transmission spectra of bulk glasses, while the second is focused on thin films. The input files for both cases are text formatted files with column organized data: wavelength or wavevector, separator (space, tab, or other) and transmission both in direct or reverse order (headers and footers are cut automatically; point, not comma should be used as decimal separator; make sure your Windows decimal separator is set to "."). This format is typical output file of most standard spectrometers. The output files from Parav are generated in text format, which can be directly read into others software, such as MicroCal Origin, Microsoft Excel, etc.

After the appropriate sub program is chosen (bulk or thin films) the input file with transmission data $T(\lambda)$ is opened. In the case of thin films the file with data on the position of the maxima and minima of the fringes can either be opened from a location (if the data are available)

or the positions can be picked manually from the transmission spectrum (do not skip minimum between two selected maxima or vice versa, since this will create error in envelop curves). These data are used for calculation of film thickness and refractive indexes n (including n_{633} at λ = 633 nm). There is a provision in the program, in case there are less than seven fringe minima, the program automatically adds points in between (by linear approximation) to improve the Cauchy's dispersion formulae, which can be set up to 10-order polynom by the user (up to 5 order polynom in the case of envelope approximation). "T_s-T tolerance" parameter determines the deviation from substrate transmission (T_s) when program starts to use formula for weak/medium absorption instead of formula for fully transmitting (negligible absorption) region. Parameters n_0 and n_s are the refractive indices of the environment (generally air) and substrate, respectively. On pressing the "Calculate" button, the program calculates the refractive index as a function of wavelength and also fits the Cauchy's dispersion formula to the estimated values, transmission (including maxima and minima envelopes) and the absorption coefficient as a function of energy. In semiconductors, the optical band gap is normally estimated from the Tauc plot [7]. The program can calculate the Tauc plot and can be chosen by clicking at the appropriate box. To calculate the optical gap, appropriate range of Tauc plot should be set either by choosing the linear region by selecting either the appropriate photon energy (x-axis) or the $(\alpha h\nu)^{1/2}$ range. After clicking the "E_g calculation" button, a linear fitting is done to the selected region in photon energies axis and the program estimates the value for E_g (intercept on x-axis) and the value of the optical bandgap E_g is also displayed in the left section of the front page. All the graphs can be scaled, moved (right click and hold), switched to autoscale (double click) and the y-axes can be interchanged, by left clicking, between linear and logarithmic scales. Once all the calculations are done, the output of each calculation and fitting can be saved by clicking the "Save results" button and the data are saved as .txt files. The same features are also available for bulk samples, but in that case the reflection spectrum $R(\lambda)$ (or constant value R) or refractive index n at λ = 633 nm should be known. The lambda/wavevectors ranges and steps of $T(\lambda)$ and $R(\lambda)$ spectra can be different. The program will automatically determine these values for further calculations.

3. Theory description

Transmission of thin homogeneous film deposited on a transparent substrate is a complex function of α, λ, n, n_s, n_0 and film thickness (d): $T = T(\alpha, \lambda, n, n_s, n_0, d)$ or in terms of absorbance $x(\lambda) = \exp(-\alpha d)$ [5]

$$T = \frac{A'x}{B' - C'x + D'x^2} \quad , \tag{1}$$

where A', B', C', D' are the complex functions of n, n_s, n_0, λ and d.

Depending on the value of x, the transmission spectrum $T(\lambda)$ can be arbitrary divided (Fig. 1) into transparent region (x = 1), region of weak/medium absorption (x < 1) and region of strong absorption (x << 1). If T_s is transmittance of a substrate; $T_s = 2n_s/(n_s^2 + 1)$, where n_s is the refractive index of the substrate, then T-T_s tolerance (can be tuned manually in the program) determines the lowest λ value (Fig. 1) at which one still wishes to use the formula for fully transmitting region. Beyond this region (T-T_s greater than tolerance value), theory for weak/medium absorption region is used for calculations.

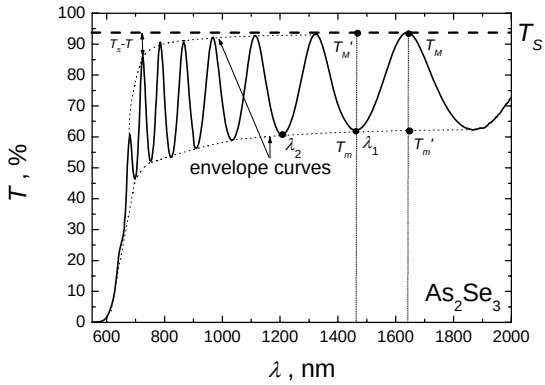

Fig. 1. Transmission spectrum of As_2Se_3 thin film (1 μm).

Solving the equation (1), in the transmitting region ($\alpha \approx 0$; $x \approx 1$), we get [5]

$$T = \frac{A}{B - C\cos\varphi + D} \quad , \tag{2}$$

where $A = 16n^2n_s$; $B = (n + n_0)^3(n + n_s^2)$; $C = 2(n^2 - n_0)(n^2 - n_s^2)$; $D = (n - n_0)^3(n - n_s^2)$ and $\varphi = 4\pi nd/\lambda$.

The interference fringes observed in this region of the transmission spectra $T(\lambda)$ of thin films can be used to determine their thickness. From the experimental data of minima of fringes (λ_1 and λ_2 corresponding to adjacent minima in $T(\lambda)$ spectrum, as shown in Fig. 1), the film thickness, d is estimated as:

$$d = \frac{\lambda_1\lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} , \tag{3}$$

where n_2 and n_1 are the values of refractive index at wavelengths λ_2 and λ_1, respectively.

The dispersion of refractive index n is calculated from fringes data (experimentally observed peaks and valleys of $T(\lambda)$ spectrum) in the fully transmitting region and the

weak/medium absorption regions using Swanepoel's theory [5].

$$n = \left[M + \left(M^2 - n_s^2\right)^{1/2}\right]^{1/2}, \tag{4}$$

where

$$M = \frac{2n_s}{T_m} - \frac{n_s^2 + 1}{2}, \tag{5}$$

T_m, T_M are the experimental values of transmission at minimum or maximum points of a particular fringe.

In weak and medium absorption region equation (5) is replaced with

$$M = 2n_s \frac{T_M - T_m}{T_m T_M} + \frac{n_s^2 + 1}{2} \tag{6}$$

where T_M and T_m should correspond to the same λ of a particular fringe (pairs T_m and T_M' or T_m' and T_M in Fig. 1) [5].

To calculate T_M' and T_m' values, an enveloping of the peaks (maxima) and the valleys (minima) was done and the envelope curves were generated using a polynomial of up to 5th order.

For extrapolation of refractive index into the regions of strong absorption, Cauchy's dispersion formulae of the polynom of $1/\lambda^{2z}$ ($Z = 0, 1, \ldots N$) type is used:

$$n = \frac{A_0}{\lambda^0} + \frac{A_1}{\lambda^2} + \ldots + \frac{A_z}{\lambda^{2z}} \tag{7}$$

where, A_i are the coefficients determined from polynomial fit [8] of n values calculated according to (4) from experimental fringes data.

Using the estimated values of refractive index and the thickness, absorption coefficient (α) as a function of photon energy ($h\nu$) is calculated using the standard equation for an absorbing thin film on a transparent substrate [9,10]:

$$\alpha = \frac{1}{d} \ln \frac{(1 - R_1)(1 - R_2)(1 - R_3)}{T}, \tag{8}$$

where R_1, R_2, R_3 are the reflection coefficients at the interfaces between surrounding medium (air)-thin film, thin film-substrate and substrate-surrounding medium (air), respectively. It is assumed here that the other multi reflections from interfaces are very small and thus can be neglected.

For the case when $n^2 >> k^2$, where $k = \alpha\lambda/4\pi$ is the absorption index, the reflection coefficients can be estimated using Frenel's formula for normal incident of light [9,10]:

$$R_1 = \left(\frac{n - n_0}{n + n_0}\right)^2 \tag{9}$$

$$R_{12} = \left(\frac{n - n_s}{n + n_s}\right)^2 \tag{10}$$

$$R_2 = \left(\frac{n_s - n_0}{n_s + n_0}\right)^2 \tag{11}$$

where n_0, n and n_S are the refractive indices of the surrounding medium (for air $n_0 = 1$), thin film (estimated using Eq. 4) and the substrate, respectively.

Equation (8) gives a reasonable accuracy for the extraction of α at least in spectral region $h\nu \le E_g$ [9]. To get a more accurate value, it is important to measure the reflection at the interface of the surrounding environment-thin film, or assumed to be constant as a function of wavelength (as in the case of most amorphous semiconductors within the transparent region). In this program this possibility is realized by checking the "use n = to calculate the absorption coefficient and thickness" box.

In the case of bulk glasses, while $\alpha d > 1$ condition is fulfilled, instead of the equation (8), the following approximation [9] gives a better result

$$\alpha = \frac{1}{d} \ln \frac{(1 - R)^2}{T} \tag{12}$$

where

$$R = \left(\frac{n - n_0}{n + n_0}\right)^2, \tag{13}$$

n is the refractive index of the bulk and n_0 is the refractive index of the medium (air).

Alternatively, if the reflection spectrum is also measured, then R can be input as experimentally measured $R(\lambda)$ spectrum. The value of R can also be fixed over a region of wavelength, as in the case of most chalcogenides, which are characterized by almost constant R in the fundamental absorption edge region [11].

The value of optical gap E_g is calculated using well-known Tauc plot [7] for indirect bandgap semiconductors (allowed transitions) as the intersecting point with $h\nu$ axis at $\alpha = 0$ after a liner fit is made to the $(\alpha h\nu)^{1/2}$ vs. $h\nu$ curve in the medium to high absorption region using the Tauc equation:

$$(\alpha h\nu)^{1/2} = B^{1/2}(h\nu - E_g) \tag{14}$$

In the case of direct bandgap semiconductors, the equation used is

$$(\alpha h\nu)^2 = A^2(h\nu - E_g) \quad (13)$$

To use Parav for direct bandgap semicondctors, the selection can be made by clicking on the box "Direct bandgap semiconductor".

4. Examples and error analysis

To show the utility of the developed program, Parav, as an example, the absorption coefficient spectra, dispersion of refractive index and Tauc plots calculated from transmission spectra of bulk sample of As_2S_3 (1 mm thickness) and thin film of As_2Se_3 (1 μm thickness deposited on a glass substrate) are shown in Figs. 2 and 3, respectively.

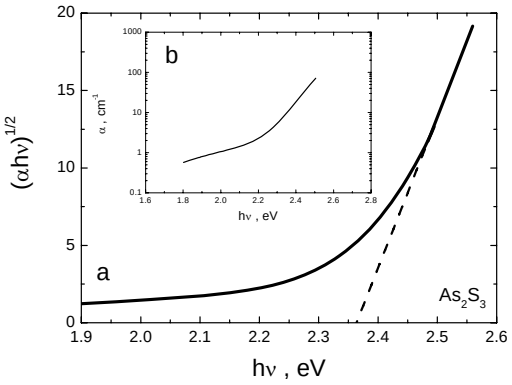

Fig. 2. Tauc plot (a) and absorption coefficient (b) of bulk vitreous As_2S_3, calculated using the program.

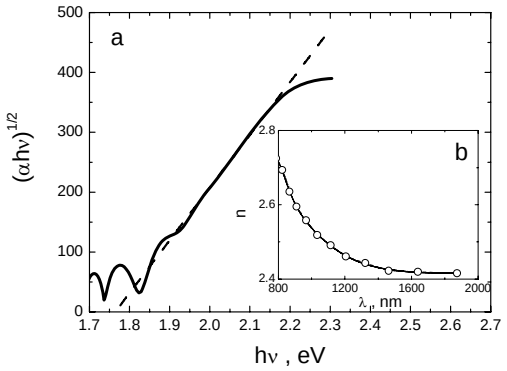

Fig. 3. Tauc plot (a) and dispersion of refractive index (b) of vitreous As_2Se_3 thin film (1 μm) on a glass substrate, calculated using the program.

Calculated E_g values (2.37 eV for bulk As_2S_3 and 1.76 eV for thin film of As_2Se_3) are in good agreement with those obtained by other authors using different approaches of estimation [11,12]. Estimated thickness of thin film (~1.01 μm) is almost the same as the thickness value obtained from the profilometry on the same samples. The error in the obtained optical constants depends mostly on the error of refractive index and thickness estimation, which, in turn, depends on the fringes data quality [5]. To show the validity of the program in other materials as well, the estimated parameters from the transmission spectra of a-Si:H thin films deposited on a glass substrate are shown in Fig. 4. The obtained values of optical gap (1.70 eV) and refractive index dispersion are also in good agreement with those reported in the literature [13].

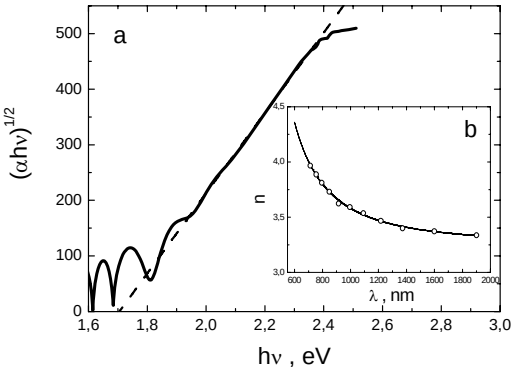

Fig. 4. Tauc plot (a) and dispersion of refractive index (b) of a-Si:H thin film, calculated using the program.

Thus, **"PARAV"** program can successfully be applied for the calculation of optical constants for a much greater number of materials.

The program can be downloaded from our website (**www.chalcogenide.eu.org,** choose in left menu "Software") free of cost and used freely. However, we would appreciate greatly if you acknowledge the efforts.

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