Optical characterization of dielectric and semiconductor thin films by use of transmission data

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A method to calculate the optical functions $n(\lambda)$ and $k(\lambda)$ by use of the transmission spectrum of a dielectric or semiconducting thin film measured at normal incidence is described. The spectrum should include the low-absorption region and the absorption edge to yield the relevant optical characteristics of the material. The formulas are derived from electromagnetic theory with no simplifying assumptions. Transparent films are considered as a particular case for which a simple method of calculation is proposed. In the general case of absorbing films the method takes advantage of some properties of the transmittance $T(\lambda)$ to permit the parameters in the two regions mentioned above to be calculated separately. The interference fringes and the optical path at the extrema of $T(\lambda)$ are exploited for determining with precision the refractive index and the film thickness. The absorption coefficient is computed at the absorption edge by an efficient iterative method. At the transition zone between the interference region and the absorption edge artifacts in the absorption curve are avoided. A small amount of absorption of the substrate is allowed for in the theory by means of a factor determined from an independent measurement, thus improving the quality of the results. Application of the method to a transmission spectrum of an a:Si_xN_{1-x}:H film is illustrated in detail. Refractive index, dispersion parameters, film thickness, absorption coefficient, and optical gap are given with the help of tables and graphs. © 1998 Optical Society of America

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1. Introduction

The optical characterization of a thin film by transmission and reflection measurements is a well-known problem. Rigorous expressions for the transmittance T and the reflectance R of a thin uniform film with smooth interfaces and of constant thickness deposited onto a transparent substrate were established by Heavens.[1] Once the experimental values of R and T are known, the mathematical problem consists in the calculation of the real and imaginary parts, n and k, respectively, of the complex refractive index of the film. A difficulty is that the expressions cannot be inverted to permit the direct calculation of n and k from the experimental values of R and T. As a consequence many numerical and graphic methods were developed to facilitate the resolution of the equations.

Another mathematical inconvenience in the resolution of the coupled equations that contain R and T is the appearance of a multiplicity of solutions n, k for a single pair of experimental values R, T.[2–7] Several criteria are used for selection of the best solution, but when the solutions are too similar the choice is difficult. The use of the optical path instead of the physical thickness, as proposed in Ref. 7, drastically reduces the number of multiple solutions, facilitating the choice of the best one.

To perform the calculations, one needs to know the value of the film thickness one needs to know but an accurate value of this parameter, compatible with the intended accuracy of the results, is frequently difficult to obtain. Furthermore, to avoid errors owing to inhomogeneity in film thickness, one needs to make an independent measurement of the thickness exactly in the same place where the light beam passed.

The simplicity of measuring the transmittance and the better accuracy of this measurement with respect to the reflectance suggest the convenience of the use of a single transmission spectrum for calculation of n and k. Swanepoel[8] followed this idea to develop his method.

In this paper I describe a new method of calculation of n, k, and the film thickness of dielectric and semiconducting thin films deposited onto transparent or semitransparent substrates by using transmission

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spectra measured at normal incidence. This choice of incidence direction is justified because no polarization effects appear; moreover, most commercial equipment uses this incidence direction. This method was applied in the laboratories of the Institute of Physics of the University of Campinas, Brazil to several kinds of material such as amorphous silicon and germanium and related compounds, III–V amorphous semiconductors, polymer films of different compositions, electrochromic oxides, and a few crystalline semiconducting films.[9–17]

The mathematical procedures used in this study make use of some properties of the transmittance that permit the separate calculation of the optical parameters in two regions: the low- and the high-absorption regions, respectively. The interference fringes of the low-absorption region are used to calculate the refractive index (real and imaginary parts) and the film thickness. In this region the small absorption is not neglected, so the accuracy of these results is improved. The film thickness thus obtained improves the precision of the results compared with those from methods that use thickness measured by an independent method. The dispersion of $n(\lambda)$ is determined in this region as well, permitting the parameterization of this function by means of any of the available models.

The absorption coefficient is computed at the absorption edge by use of the results of the low-absorption region. Spurious modulations or peaks usually observed in the absorption coefficient curve are eliminated by judicious correction of the refractive index.

A theoretical background is included in Section 2 to facilitate the explanations of the mathematical procedures. Transparent films are treated in Section 3 as a special case. A simple method for the determination of the refractive index and the film thickness is developed for this case. In this section, and in Section 4 as well, the experimental data of an a-$\mathrm{Si}_x\mathrm{N}_{1-x}$:H film are used to show the different calculations. Section 4 describes the calculations of the absorbing film, giving the results of the absorption coefficient and the optical gap of our particular example. Discussions of the accuracy and the applicability of the method are contained in Section 5. Some recommendations on the properties of samples to be characterized are given as well. The appendixes contain the formulas for the transmittance and reflectance of both transparent and semi-transparent substrates, which are useful for completion of the data necessary to optimize the results.

2. Theoretical Background

The formulas used in the calculation of the optical parameters of a thin film deposited onto a thick substrate that use experimental transmission spectra should include the reflections from the second interface of the substrate; otherwise the results will be affected by systematic and significant errors.[7,8]

The derivation of the expressions for the transmittance and reflectance is made in two steps. The first one gives the well-known transmittance and reflectance of the film with smooth and parallel faces bounded by two semi-infinite media.[18] In the second step the multiple incoherent reflections from the substrate–air interface are included to yield the final expressions.

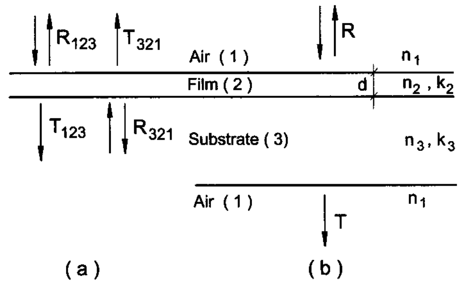

Fig. 1. Optical parameters and directions of the transmittance and reflectance adopted for the film–substrate assembly: (a) semi-infinite substrate, (b) finite substrate.

To permit the characterization of both transparent and absorbing films, a complex refractive index of the film is used throughout this study. The analysis of the optical spectrum of the sample, which usually includes the interference fringe region and the absorption edge, yields the refractive index and the absorption coefficient of the film. The thickness of the thin film is also obtained, frequently with a better precision than for the result obtained from an independent measurement.

For the first step of the calculation (semi-infinite substrate) we consider a film of complex refractive index $N_2 = n_2 + ik_2$ and thickness d, bounded by two semi-infinite transparent media of real refractive indices $N_1 = n_1$ and $N_3 = n_3$; see Fig. 1(a). Usually the incident medium is air with $n_1 = 1$.

The amplitudes of the reflected and the transmitted electric fields with respect to the incident field at each interface ij are given by the corresponding Fresnel coefficients:

$$r_{ij} = \frac{N_i - N_j}{N_i + N_j}, \qquad t_{ij} = \frac{2N_i}{N_i + N_j}. \tag{1}$$

The refractive indices $N_j = n_j + ik_j$ with $j = 1, 2, 3$ correspond to the incident medium, film, and substrate, respectively, according to Fig. 1.

The amplitudes of the electric field of the waves transmitted and reflected by the film are given by the following coefficients, where both incidence directions, (123) and (321), are considered:

$$t_{123} = \frac{t_{12}t_{23} \exp(i\Psi/2)}{1 + r_{12}r_{23} \exp(i\Psi)}, \tag{2}$$

$$t_{321} = \frac{t_{32}t_{21} \exp(i\Psi/2)}{1 + r_{32}r_{21} \exp(i\Psi)}, \tag{3}$$

$$r_{123} = \frac{r_{12} + r_{23} \exp(i\Psi)}{1 + r_{12}r_{23} \exp(i\Psi)}, \tag{4}$$

$$r_{321} = \frac{r_{32} + r_{21} \exp(i\Psi)}{1 + r_{32}r_{21} \exp(i\Psi)}, \tag{5}$$

where the phase difference of the wave between the two interfaces $\Psi/2$ of the film is defined by

$$\psi = 4\pi N_2 d/\lambda \tag{6}$$

and λ is the vacuum wavelength of the light.

The complex angle Ψ is separated into its real and imaginary parts:

$$\mathrm{Re}(\Psi) = 4\pi n_2 d/\lambda = \varphi, \tag{7a}$$

$$\mathrm{Im}(\Psi) = 4\pi k_2 d/\lambda = \alpha d. \tag{7b}$$

$\alpha = 4\pi k_2/\lambda$ is usually called the absorption coefficient of the film; φ is referred to as the phase angle.

The values of the reflectance and the transmittance of the film, according to electromagnetic theory, are defined by

$$R_{123} = r_{123} r_{123}^*, \tag{8}$$

$$R_{321} = r_{321} r_{321}^*, \tag{9}$$

$$T_{123} = (n_3/n_1) t_{123} t_{123}^*. \tag{10}$$

The transmittances in both directions are equal when the substrate is transparent.

The effect of the finite substrate [see Fig. (1b)], is introduced, according to Knittl,[19] by means of the following expressions, which are valid for transparent and weakly absorbing substrates:

$$R = \frac{R_{123} + ({T_{123}}^2 - R_{123}R_{321})\rho U^2}{1 - \rho R_{321} U^2}, \tag{11}$$

$$R' = \frac{(1 - 2\rho)R_{321}U^2 + \rho}{1 - \rho R_{321} U^2}, \tag{12}$$

$$T = \frac{(1 - \rho)T_{123}U}{1 - \rho R_{321} U^2}. \tag{13}$$

R and R' are the reflectances in the (123) and (321) directions, respectively, and T is the value of the transmittance of the assembly (film + substrate), according to Fig. (1b). Any weak absorption in the substrate is taken into account by the factor U, which can be determined separately as indicated in Appendix B. The factor

$$\rho = [(n_1 - n_3)^2 + {k_3}^2]/[(n_1 + n_3)^2 + {k_3}^2]$$

is the reflectivity of the 1–3 interface. Usually, in the substrates used for transmission experiments, the absorption is zero or small; in these cases the term ${k_3}^2$ can be dropped.

Substituting R_{321} and T_{123} from Eqs. (9) and (10), respectively, into Eq. (13) and after a straightforward but tedious calculation, one gets for the transmittance

$$T = \frac{A \exp(\alpha d)}{B \exp(2\alpha d) + C \exp(\alpha d) + D}, \tag{14}$$

where A, B, C, and D (given in Appendix A) are algebraic functions of the optical constants and thickness of the film and adjacent media. In the low-absorption region of the spectrum the factor C in Eq. (14) is responsible for the modulation of the transmittance [see Eq. (A3) below]. Equation (14), which does not involve any approximation, is used throughout this study and applied to the different regions of the spectrum, independently of the intensity of the absorption.

Table 1. Determination of Refractive Index n_2 and Film Thickness d of an a-Si_xN_{1-x} Film by the Method of Section 3 (Transparent Film)

λ (nm)	m	n_3	T_{odd}	n_2	d (nm)
1887	3	1.462	0.8034	1.881	753
1149	5	1.464	0.7976	1.898	757
823.0	7	1.468	0.7912	1.919	756
645.2	9	1.473	0.7843	1.941	748
531.9	11	1.479	0.7761	1.967	744
435.5	13	1.486	0.7669	1.997	738
392.6	15	1.494	0.7550	2.036	732
355.2	17	1.503	0.7357	2.098	719

3. Treatment of Transparent Films

The simplest case of thin-film calculation with a transmission spectrum occurs when interest is limited to a region where absorption can be neglected. The sequence of steps indicated below can be followed in Table 1, which contains the results for a silicon nitride film.

When $k_2 = 0$ the film is said to be transparent, and the fully modulated interference fringes appear. The extrema (maxima and minima) of the transmittance occur at wavelengths λ_m, which satisfy the condition[18]

$$4\pi n_2 d/\lambda_m = m\pi, \tag{15}$$

where $m = 1, 2, 3 \ldots$ are the interference orders of the fringes. Although Eq. (15) is strictly valid only for a dispersion-free film, in practice small dispersions do not invalidate the expression. At the extrema the phase angle reduces to

$$\varphi = m\pi. \tag{16}$$

Applying the above condition [Eq. (15)] to Eq. (13) or (14), one gets for the even and the odd interference orders

$$T_{\mathrm{even}} = \frac{2n_1 n_3}{{n_1}^2 + {n_3}^2}, \tag{17}$$

$$T_{\mathrm{odd}} = \frac{4 n_1 {n_2}^2 n_3}{({n_1}^2 + {n_2}^2)({n_2}^2 + {n_3}^2)}. \tag{18}$$

By comparison of Eqs. (17) and (B1) below, one sees that the transmittance of the film–substrate assembly equals the transmittance of the naked substrate at the wavelengths that correspond to the even orders. In other words, the modulated transmittance curve of the film is tangential to the flat transmission curve of the substrate at these points. Furthermore, it can be shown that $T_{\mathrm{odd}} < T_{\mathrm{even}}$ when $n_2 > n_3$, which

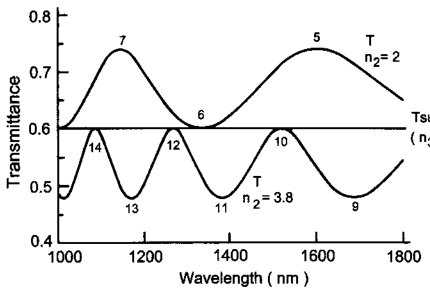

Fig. 2. Calculated transmittance of a thin transparent film when $n_2 < n_3$ (upper curve) and $n_2 > n_3$ (lower curve), showing the points where the transmittance of the film is tangential to the transmittance of the substrate (even orders of interference). The interference order m is indicated at each extremum. The refractive indices are $n_1 = 1$, $n_2 = 2$, $n_2 = 3.8$, and $n_3 = 3$.

means that the transmission curve of the assembly lies beneath the transmission of the substrate. The opposite is true for $n_2 < n_3$. These two opposite situations are demonstrated in Fig. 2. The first case, for which T_{even} corresponds to the maxima, is frequently found when a semiconducting or dielectric film is deposited onto a glass or a quartz substrate. Samples deposited upon silicon substrates for IR measurements are examples of the second case, where T_{even} are minima.

The interference orders m can be determined from Eq. (15). The dispersion of the refractive index of any dielectric or semiconductor is small in its region of transparency; therefore for any three consecutive extrema we have

$$(m-1)\lambda_{m-1} \cong m\lambda_m \cong (m+1)\lambda_{m+1}. \tag{19}$$

From Eq. (19), the following relations for the calculation of m, which can be used interchangeably, are derived:

$$m \cong \frac{\lambda_{m-1} + \lambda_{m+1}}{\lambda_{m-1} - \lambda_{m+1}},$$
$$m \cong \frac{\lambda_{m-1}}{\lambda_{m-1} - \lambda_m},$$
$$m \cong \frac{\lambda_{m+1}}{\lambda_m - \lambda_{m+1}}. \tag{20}$$

A few consecutive values of m are determined, preferably at the long-wavelength side of the spectrum where the precision of relations (20) is better; then the rest of the sequence, for the remaining extrema, is reliably assigned. Some remarks about the determination of the values of m are useful at this point: (a) In the assignment of the interference orders the parity of m should always be observed; i.e., the order of the extrema where the transmission of the film touches the transmission of the substrate should be even numbers. (b) Small values of m are found in thinner films; if this is the case ($m < 15$) the uncertainty of m as determined by relations (20) is small. (c) If $m > 15$, greater uncertainties may arise, which could induce the operator to accept two m sequences instead of a single one, for instance, $m = 20, 22, 24, \ldots$ and $m = 22, 24, 26, \ldots$ for the same set of even-order extrema. If this is the case, the uncertainty in m will be reflected in the error of the refractive index and of the film thickness calculated thereafter.

The optical path in the film at each λ_m as determined from Eq. (15),

$$s(\lambda_m) = dn_2(\lambda_m) = m\lambda_m/4, \tag{21}$$

is known from the experimental spectrum. It will help in the complete determination of the refractive index.

We calculate the refractive index of the film at the odd-order extrema, using the experimental values T_{odd}. From Eq. (18) we get a biquadratic equation in n_2 whose positive roots are

$$n_2 = [\beta \pm (\beta^2 - n_1^{\,2} n_3^{\,2})^{1/2}]^{1/2}, \tag{22}$$

where

$$\beta = \frac{2n_1 n_3}{T_{\text{odd}}} - \frac{n_1^{\,2} + n_3^{\,2}}{2}. \tag{23}$$

When the transmission spectrum imposes the condition that $n_2 > n_3$, only one of the roots [Eq. (22)] satisfies this condition. In the opposite case both roots satisfy the condition $n_2 < n_3$; then, we need additional information to find the best solution: an additional measurement changing n_1 (a liquid instead of air, for instance) or an additional sample deposited onto a substrate with different n_3.

Knowledge of n_2 at the odd orders and the optical path [Eq. (21)] at these points allows one to calculate a set of values of d, the mean value of which is adopted as the film thickness. Finally, at the even-order extrema, n_2 is determined by means of the optical path and the film thickness already determined. With this step the calculation of the refractive index of the transparent film at the initially selected extrema is completed.

Frequently a model function for the refractive index is needed, as is shown in Section 4. We choose the single-oscillator model that is due to Wemple and Didomenico[20] (W-D) in which the dispersion of the refractive index is related to the photon energy, $E = hc/\lambda$, according to the equation

$$n^2(E) = 1 + \frac{E_m E_d}{E_m^{\,2} - E^2}, \tag{24}$$

where the parameters E_m and E_d are the oscillator and the dispersive energies, respectively. We can easily determine these parameters by plotting $(n^2 - 1)^{-1}$ versus E^2. This procedure gives statistically significant results whenever the number of extrema is not small.

To illustrate this procedure we use transmission data of a hydrogenated amorphous silicon–nitrogen compound deposited onto a quartz substrate. Figure 3 shows the complete spectrum as measured with a Perkin-Elmer Lambda 9 spectrophotometer. The near-infrared, visible, and ultraviolet ranges were

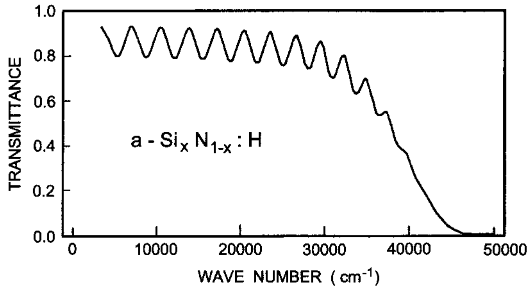

Fig. 3. Experimental transmission spectrum of an a-Si$_x$N$_{1-x}$:H film, showing the interference (low-absorption) region and the absorption edge. The transmission is plotted as a function of the wave number to show the details of the absorption edge.

covered in the measurement. The film will be considered absorptionless for the purpose of this section in the wavelength interval from 400 to 2000 nm. Table 1 shows the results of the present calculations: the interference orders, the refractive index n_2, and the thickness d at the minima (odd-order extrema) are determined by means of relations (20) and Eqs. (22) and (15), respectively. The refractive index of the substrate was computed from its transmittance with the assumption that it has zero absorption [Eq. (B3)] below. No problems arise in determination of the values of m in this film because the uncertainties of the results of relations (20) are so small.

The material of the film characterized in this section is not completely transparent in the chosen spectral range. The effects of this small absorption are a systematic error in the refractive index and a deviation of the film thickness as a function of the wavelength, as is illustrated in Table 1. The best values of n_2 and d correspond to the smaller orders where the absorption is quite small.

4. Treatment of Absorbing Films

The calculation of the real or the imaginary parts of the refractive index of the film with a given experimental value of the transmittance is done numerically by means of the equation

$$T(n_2, k_2, \lambda, d, n_1, n_3) - T_{\exp} = 0, \tag{25}$$

where either n_2 or k_2 is chosen as an unknown. One can use any efficient root-finding procedure to determine the desired parameter. The analytical expression for the transmission to be used in Eq. (25) is given by Eq. (14) with Eqs. (A1)–(A4) in Appendix A. An alternative, and computationally faster, method to determine k_2 (or α) is as follows: Eq. (14) is rearranged to give

$$\exp(\alpha d) = \frac{1}{2B}\left\{\left(\frac{A}{T_{\exp}} - C\right) + \left[\left(\frac{A}{T_{\exp}} - C\right)^2 - 4BD\right]^{1/2}\right\}, \tag{26}$$

where the exponential dependence on α is now isolated. We determine an approximate value of $\exp(\alpha d)$ by calculating the second member of Eq. (26), using an arbitrary value of k_2 (or α). This result is used to repeat the calculation with the new value of k_2 [Eq. (7b)]. The repetition of this procedure results in an efficient iterative method that converges rapidly. Three or four iterations are sufficient to yield a value of the absorption coefficient with satisfactory precision.

Here, for the purpose of the calculation, we divide the spectrum into two parts: the low-absorption region, where the interference dominates with the typical fringes produced by the coherent reflections at the interfaces of the film, and the absorption edge, where the abrupt increase in the light absorption causes the simultaneous diminution of the modulation of the fringes and of the absolute intensity of the transmitted radiation until it becomes negligible. These two regions are treated separately.

A. Low-Absorption Region

Here we calculate the refractive index and the absorption coefficient at the maxima and minima of the transmission in the interference region. This part of the calculation parallels the procedure followed in Section 3, with the difference that the absorption is not ignored.

This calculation is simplified by consideration of two properties of the transmission:

(1) Equation (15), which states the condition for the occurrence of maxima and minima in the transparent films, is approximately true in absorbing films too, with the condition that the interference fringes be neatly defined.[7] Then we can define and calculate the interference orders m and set the values of the phase angle $\varphi = m\pi$ at each λ_m, as was done in Section 3, even if the film is not strictly transparent.

(2) The value of the transmittance at the even-order extrema depends strongly on k_2 but only weakly on n_2. Consequently, by use of an approximate value of the refractive index n_2 it is possible to determine reasonably accurate values of the extinction coefficient k_2 at these extrema with the help of Eq. (26). The approximate value of n_2 that is necessary for this purpose can be given by the transparent film approximation, Eq. (22). This property, in addition to the possibility of the determination of α in the low-absorption region, permits an improvement in the calculation of n_2.

In Table 2 we present the absorption coefficient at the even-order extrema (maxima of the transmission); the data correspond to those used in Section 3. The approximate values of n_2 are taken from Table 1. The calculation of α was done with Eq. (26) and condition (16); in this case we chose as the initial value $\alpha_0 = 0$, and no iteration was necessary because of the smallness of the absorption coefficient. It should be noted that in this part of the calculation knowledge of the film thickness is not needed because of the use of condition (16).

The absorption data of Table 2 permit the calcula-

Table 2. Calculation of the Absorption Coefficient of the a-Si_xN_{1-x} Film for Even Orders (Subsection 4.A, Low Absorption Region)[a]

λ (nm)	m	n_3	n_2	T_{exp}	α (cm^{-1})
1439.0	4	1.463	1.89	0.9273	56.8
961.5	6	1.466	1.91	0.9218	120.5
724.6	8	1.470	1.93	0.9163	181.1
584.8	10	1.475	1.95	0.9111	234.0
490.2	12	1.482	1.98	0.9043	306.4
424.6	14	1.490	2.02	0.8968	385.7
375.9	16	1.498	2.06	0.8828	552.0
339.0	18	1.507	2.13	0.8524	1077.0

[a]The values of n_2 were taken from Table 1.

tion of the refractive index at the odd-order extrema (minima of transmission) by numerical solution of Eq. (25). It is expected that these n_2 will be better that those of Section 3, where the absorption was not taken into account. These results are shown in Table 3, where the rightmost column contains the value of the thickness obtained from Eq. (15) at each minimum. As expected, the spread of the values of d is much smaller than that in Table 1. The mean value is $d = 760 \pm 2$ nm.

So far we have obtained the values of n_2 only at odd orders, but knowledge of the thickness permits determination of n_2 at the even orders as well. These values are not included in Table 3.

The complete set of refractive indices (at even and odd orders) is plotted in Fig. 4 as a function of the photon energy. The inset shows the W-D plot used in determining the parameters of the model: $E_d = 23.7 \pm 0.3$ eV and $E_m = 9.28 \pm 0.01$ eV. The small amount of spread that we can observe in Fig. 4

Table 3. Calculation of Refractive Index n_2 and Thickness d for the Odd Orders (Subsection 4.A)[a]

λ (nm)	m	T_{odd}	n_2	d (nm)
1149	5	0.7976	1.886	762
823.0	7	0.7912	1.901	758
645.2	9	0.7843	1.916	758
531.9	11	0.7761	1.928	759
435.5	13	0.7669	1.939	760
397.6	15	0.7555	1.953	763
355.2	17	0.7357	1.991	758

[a]The values of α were obtained from Table 2 by interpolation.

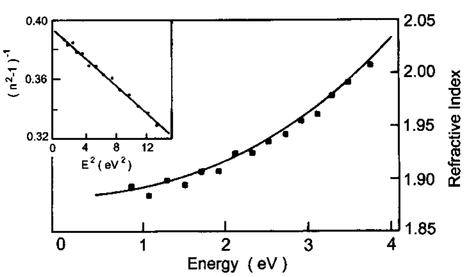

Fig. 4. Refractive index of the film of Fig. 3, including the experimental points and the W-D fitting. Inset, W-D plot used in determining the parameters E_m and E_d of the model.

Table 4. Calculation of the Absorption Coefficient at the Absorption Edge (Subsection 4.B)

λ (nm)	E (eV)	U	T_{exp}	α (cm^{-1})
339.0	3.658	1	0.8524	926
309.6	4.005	1	0.8004	1 651
287.4	4.315	1	0.6981	3 227
269.5	4.600	0.9930	0.5546	5 550
246.9	5.022	0.9545	0.2661	13 930
241.0	5.146	0.9404	0.2004	17 300
235.3	5.270	0.9437	0.1380	22 520
229.9	5.394	0.9621	0.0906	27 900
224.7	5.518	0.9642	0.0528	35 230
219.8	5.642	0.9458	0.02679	43 660
215.1	5.766	0.9209	0.01122	54 760
210.5	5.890	0.8895	0.00372	68 710
206.2	6.014	0.8569	0.00100	85 420
202.0	6.138	0.8341	0.00026	102 800

is reflected in the smallness of the errors of E_m and E_d, demonstrating the applicability of the model. The results of this section are used in Subsection 4.B to characterize the absorption edge.

B. Optical Absorption Edge

When the absorption increases at the absorption edge, the number of multiply reflected beams that effectively contribute to the transmitted light diminishes gradually until the interference becomes irrelevant. Simultaneously the intensity of the transmitted light decreases rapidly, as can be seen from Fig. 3.

The iterative procedure associated with Eq. (26) is adopted to compute the absorption coefficient. For this purpose it is necessary to know at each wavelength the transmittance, the refractive index of the substrate, and the refractive index of the film and its thickness as determined in the low-absorption region. Absorption in the substrate is taken into account by means of the factor U introduced in Eqs. (11)–(13), which can be evaluated by means of the transmission of the substrate, Eq. (B6) below.

Selected values of α as a function of the photon energy are contained in Table 4. The quartz substrate of this sample is partially absorbing in part of the ultraviolet region. The values of U that we used to correct this effect are included in that table. Figure 5 shows the absorption coefficient as a function of energy. The graph includes the results at the absorption edge and in the low-absorption region.

At the higher-absorption end of the spectrum, where no traces of interference are found, the transmittance is a monotonically increasing curve. In this range a smooth curve for α is always obtained. On the other hand, the transmittance in the transition region, where the interference effects are still present, is slightly modulated. In this part of the spectrum the α-versus-E curve may show some spurious peaks or modulations because of the use of an incorrect refractive index in the calculation. This effect appears because the refractive index given by the W-D model may be different from the true val-

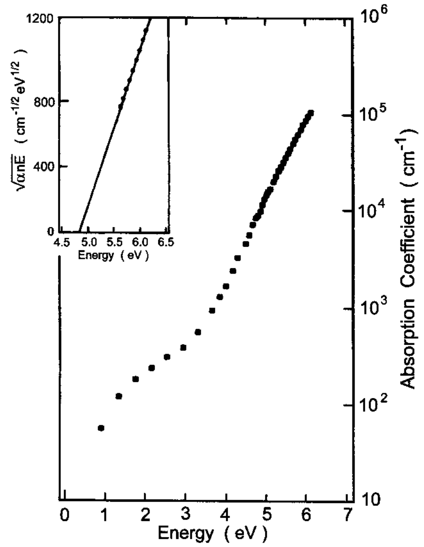

Fig. 5. Absorption coefficient of the film of Fig. 3. The results cover the low-absorption region and the absorption edge. The Tauc plot for the determination of the optical gap is shown in the inset.

ues at the absorption edge. One can easily correct this artifact by changing the parameters of the model slightly, as was done in the treatment of our data, thus yielding a rather smooth curve in the interval from 4 to 5 eV where the spurious peaks are expected.

The study of the absorption edge is important for an understanding of the mechanisms of optical absorption in crystalline and amorphous materials. It is of great practical interest because knowledge of the absorption coefficient in this region permits the determination of the optical gap, one of the most important optical properties of the material. The shape of the absorption edge and the determination of the optical gap depend strongly on the electronic structure of the material.[21–23] In our case the sample is a wide-gap amorphous semiconductor, which is expected to show a subbandgap absorption region, an Urbach tail with an exponential increase in absorption, and a Tauc region that one can use to determine the optical gap in this material. These three regions are seen in Fig. 5 and occupy roughly the energy intervals (1, 3.5), (3.5, 5.5), and (5.5, 6.2) eV, respectively.

We can express the absorption in the Urbach tail by the equation

$$\alpha = \alpha_0 \exp(E/E_0). \tag{27}$$

The values of the parameters of Eq. (27) that correspond to the results of Fig. 5 are $E_0 = 485 \pm 3$ meV and $\alpha_0 = 0.43 \pm 0.03$ cm^{-1}.

According to Tauc,[23] in amorphous materials the absorption that is due to the band-to-band transitions that determine the optical gap E_g is given by

$$E\sqrt{\varepsilon_2} = \gamma(E - E_g), \tag{28}$$

where ε_2 is the imaginary part of the dielectric function. Introducing the absorption coefficient transforms Eq. (28) into

$$\sqrt{\alpha n E} = \beta(E - E_g), \tag{28$'$}$$

where β is a constant related to the structure of the amorphous material. This theory predicts an energy interval where the experimental values have the linearity established by Eq. (28) and thus permits the determination of the optical gap. The inset of Fig. 5 is a Tauc plot from Eq. (28′) with the parameters $E_g = 4.83 \pm 0.13$ eV and $\beta = 971 \pm 16$(eV cm)$^{-1/2}$.

The determination of E_g by the Tauc method requires the measurement of quite small transmittances to yield the linear part of the plot, as can be seen from the bottom few rows of Table 4.

5. Discussion and Comments

The method of optical characterization of thin films discussed in this paper has the following features:

(1) From the theoretical point of view, all the formulas were rigorously derived from electromagnetic theory. No approximations were introduced to facilitate the calculations. As a consequence, the same formulas are used in the different regions of the spectrum, avoiding errors and simplifying the programs used for the calculations.

(2) The interference fringes are fully used in the transparent region and in the spectral region with weak absorption. Accurate results of the refractive index and its dispersion (from the W-D model, for instance) are obtained in these two spectral regions.

(3) The absorption coefficient in the low-absorption region (subgap absorption) can be obtained with reasonable precision if appropriate values of the refractive index and absorption of the substrate are introduced into the formulas.

(4) An accurate value of the film thickness is obtained from the interference fringes of the spectrum as an important by-product of the calculations. Allowance for the absorption of the substrate improves the accuracy of both film-thickness and refractive-index results.

(5) Undesirable spurious peaks of the absorption coefficient curve in the transition zone lying between the absorption edge and the fringe region are avoided by the adjustment of the W-D parameters to produce a small variation of the refractive index in this region. A monotonically increasing α-versus-E curve is thus obtained, as shown in Fig. 5.

(6) The quality of the results was systematically verified by calculation of the transmittance spectrum by use of the calculated values of n_2(E), α(E), and d. The coincidence of experimental and calculated spectra was usually remarkable.

(7) The mathematics used in this method, in spite of the fact that the full theory is used in the derivation of the formulas, is simple enough to permit the use of a good programmable pocket calculator to per-

form all the calculations required for a complete characterization.

(8) The paper is self-contained in the sense that all necessary theoretical formulas, corresponding to both film and substrate, have been included. Detailed explanations related to the calculations of the index of refraction, absorption coefficient, film thickness, and optical gap have been given as well.

One should observe some aspects related to the samples and the substrates to optimize the result of the calculations:

(1) The films should be deposited onto thick enough substrates ($d_s > 0.4$ mm) to prevent the appearance of interference in the light owing to reflections at the interfaces of the substrate. These fringes obscure the spectrum of the film and make analysis of the data difficult.

(2) When the main purpose of the exercise is the determination of the optical gap, it is convenient to reach the highest values of the absorption coefficient permitted by the data; thinner films are better in this case. Films that are too thin, however, may produce few interference fringes, thus diminishing the accuracy of the calculated film thickness that enters into the calculation of the absorption coefficient. So a compromise between the two opposite situations has to be made.

(3) Thicker films are to be preferred in those cases in which the main interest is focused on the film's thickness, refractive index, and absorption coefficient in the low-absorption region.

(4) The uniformity of the film's thickness should be optimized in the preparation of the samples because differences in thickness in the region of the sample covered by the light beam of the spectrophotometer may modify the transmission spectrum. One can minimize the effect of small inhomogeneities by diminishing the size of the light beam used in the measurement by means of a diaphragm or a beam condenser. The latter alternative should be preferred, if available, because smaller diaphragms diminish the beam energy, impairing the signal-to-noise ratio.

(5) Precise values of the refractive index of the substrate [Eq. (B3) below] and of the absorption factor U [Eq. (B6), which is frequently not considered] are necessary for improvement of the results, especially in the low-absorption region. The well-known absorption bands in the near infrared and ultraviolet regions of glass, quartz, and other common substrates should not be forgotten.

Appendix A. Transmission of a Thin Absorbing Film Deposited onto a Thick Semitransparent Substrate

The substitution of Eqs. (9) and (10) into Eq. (13) results in a lengthy expression. We adopt the following simplifying definitions to write Eq. (14):

$$A = 16n_3(1-\rho)(n_2^2 + k_2^2)U, \tag{A1}$$

$$B = st - Usv\rho, \tag{A2}$$

$$\begin{aligned} C = {} & [2(4n_3k_2^2 - ZY)\cos\varphi + 4k_2(n_3Y + Z)\sin\varphi] \\ & - \rho U^2[4k_2(Z - n_3Y)\sin\varphi - 2(ZY + 4n_3k_2^2)\cos\varphi], \end{aligned} \tag{A3}$$

$$D = uv - U^2tu\rho, \tag{A4}$$

$$u = (n_1 - n_2)^2 + k_2^2, \tag{A5}$$

$$v = (n_2 - n_3)^2 + k_2^2, \tag{A6}$$

$$s = (n_1 + n_2)^2 + k_2^2, \tag{A7}$$

$$t = (n_2 + n_3)^2 + k_2^2, \tag{A8}$$

$$Y = n_2^2 - n_1^2 + k_2^2, \tag{A9}$$

$$Z = n_2^2 - n_3^2 + k_2^2. \tag{A10}$$

Appendix B. Transmittance and Reflectance of Transparent and Semitransparent Substrates

In the thick plates ($d_s > 0.4$ mm) commonly used as substrates for thin films, the light multiply reflected at the interfaces loses its coherence because of the irregularities of the surfaces. In this case we can calculate the total transmitted and reflected intensities by summing the partial intensities of the contributing beams.

It can be shown that in the case of transparent substrates the transmittance and the reflectance of the substrate are given by

$$T_S = \frac{1-\rho}{1+\rho}, \tag{B1}$$

$$R_S = \frac{2\rho}{1+\rho}, \tag{B2}$$

respectively, where ρ has the same definition as given in Section 3.

If the transmittance of the substrate and the refractive index of the incident medium are known, the refractive index of the substrate is determined by

$$n_3 = n_1\left[\frac{1}{T_s} + \left(\frac{1}{T_s^2} - 1\right)^{1/2}\right]. \tag{B3}$$

The equivalent expressions for semitransparent substrates are

$$T_S = \frac{(1-\rho)^2\exp(-\alpha_s d_s)}{1-\rho^2\exp(-2\alpha_s d_s)} \tag{B4}$$

$$R_S = \rho\left[1 + \frac{(1-\rho)^2\exp(-2\alpha_s d_s)}{1-\rho^2\exp(-2\alpha_s d_s)}\right], \tag{B5}$$

where α_s and d_s are the absorption coefficient and the thickness, respectively, of the substrate.

The factor $U = \exp(-\alpha_s d_s)$ introduced in Eqs. (9)–(11), which takes into account the absorption of the substrate in these equations, can be determined by means of the following equation derived from Eq. (B4):

$$U^{-1} = \frac{(1-\rho)^2}{2T_s} + \left[\frac{(1-\rho)^4}{4T_s^{\,2}} + \rho^2\right]^{1/2}. \qquad \text{(B6)}$$

To calculate U it is necessary to know n_1 and n_3 and to measure the transmittance T_s of the naked substrate.

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