Methods for the determination of the optical constants of thin films from single transmission measurements: a critical review

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Abstract
Optical transmission measurements are commonly used for the routine determination of thin film optical constants. This paper presents an overview of the different methods of evaluating these transmission data, leading to values for the complex refractive index. Three different groups of methods are distinguished using: (1) at least two different optical measurements; (2) dispersion relations or general physical constraints to approximate the behaviour of the wavelength-dependent refractive index; and (3) a 'virtual' measurement as a second variable. The methods from groups (2) and (3) (requiring only a single transmission measurement) are treated in more detail and are evaluated in terms of their accuracy.

1. Introduction

The knowledge of accurate values of the wavelength-dependent complex refractive index of thin solid films is very important, both from a fundamental and a technological viewpoint. It yields fundamental information on the optical energy gap (for semiconductors and insulators), defect levels, phonon and plasma frequencies, etc. Moreover, the refractive index is necessary for the design and modelling of optical components and optical coatings such as interference filters.

If the model of an isotropic, homogeneous and plane-parallel thin film can be adopted, the real and imaginary parts of the refractive index at each wavelength completely determine the optical properties of the film (in most instances, the film thickness can be determined at the same time). Therefore, two independent measurements are necessary at each wavelength in order to solve for the unknowns $n(\lambda)$ and $k(\lambda)$.

If the above-mentioned requirements are not met (for inhomogeneous films [1–3] or rough films [4, 5]), it is still possible in most cases to model the optical properties of the 'non-ideal' thin films, albeit with somewhat more complexity.

Numerous methods have been devised for the determination of the refractive index of thin films. Advantages and disadvantages of the most important methods will be discussed; Three different groups of methods will be distinguished using:

(1) at least two different optical measurements,
(2) dispersion relations or general physical constraints to approximate the behaviour of the wavelength-dependent refractive index and
(3) a 'virtual' measurement as a second variable.

Special attention will be given to methods, using only a single transmission spectrum (groups (2) and (3)), since these require the least experimental effort. The dependence of the results on experimental errors will not explicitly be discussed here; this has been done in detail in other studies [6–8].

2. Results and discussion

2.1. Methods using two independent measurements

Since many years, the combination of a normal incidence transmission measurement and a near-normal incidence reflectance measurement—in short the (R, T) method—has been used for the (n, k) determination [9–12]. This method

suffers a few disadvantages:

(a) It is very difficult to obtain sufficiently accurate absolute specular reflectance data. In spectrophotometric measurements, there are two common methods for measuring specular reflectance. Using the simplest experimental set-up, one measures the light attenuation upon a single reflectance at the sample surface, which is then compared to the reflectance of a calibrated mirror (see figures 1(a) and (b)). This method obviously necessitates such a calibrated mirror, which is both expensive and, moreover, only has limited shelf life: its reflectance is only guaranteed for a few months due to ageing effects. A more elegant way for measuring absolute reflectance is the VW-set-up, introduced by Strong [13] and shown schematically in figures 1(c) and (d). Here, a moveable mirror is first placed in a 'reference' position, and the corresponding combined reflectance of the two fixed mirrors and the moveable mirror is acquired. Then, the moveable mirror is switched to its 'measurement' position and the film to be investigated is mounted. Now (figure 1(d)), the only optical difference with the reference measurement (figure 1(c)) is a double reflectance off the sample under test. Thus, division of the 'measurement' and 'reference' values exactly yields the square of the reflectance needed, irrespective of the reflectance of the mirrors used. The only obvious disadvantage of the VW-method is that the two reflectances on the sample occur on different spots. Therefore, the sample should be perfectly homogeneous over at least the distance between the two spots, including the size of the beams, typically 25 mm in total [14].

(b) Usually, it is nearly impossible to measure transmittance and reflectance at exactly the same spot on the film; if the film is not perfectly homogeneous (in composition or in thickness), which is inevitable, this further decreases the overall accuracy of the method.

(c) There is no easy way to measure normal incidence reflectance. In the usual methods (described above), the angle of incidence is 7° [14]. For maximum accuracy, this angle
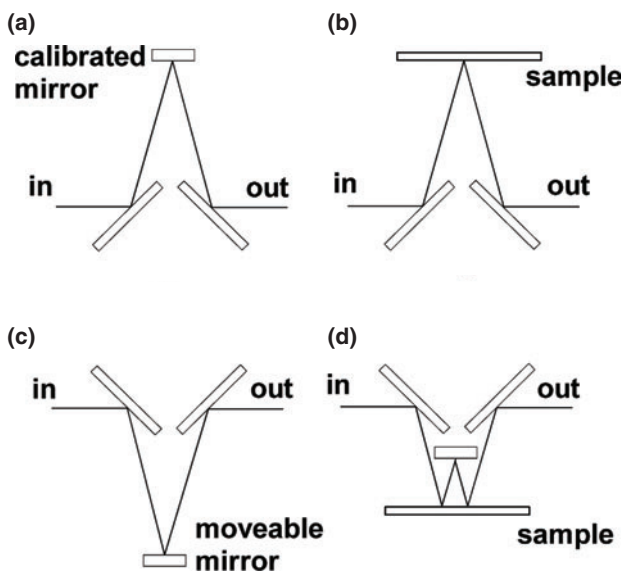

Figure 1. Experimental set-ups for measuring specular reflectance: using a calibrated mirror, in reference position (a) and measurement position (b) and using the VW-set-up, in reference position (c) and measurement position (d).

should be taken into account in the subsequent calculations. It also makes the measurements sensitive to polarization effects.

(d) The (n, k) determination from (R, T) is based on a numerical inversion. Numerous papers have been published on different inversion methods [10] and on the accuracy limits of the technique [15–17], but it usually remains a source of errors and a possibility for multiple solutions.

Remark that if the optical transmission of a thin film is extremely low due to excessive absorption, reflection measurements may be the only choice. In that case, the combination of two reflection measurements, using different incident angles and/or different polarization, can be employed.

Numerous other methods, using two different measurements, have been published. We will only sum up a few of these as examples:

(a) Transmission measurements on two films of different film thickness [18]: obviously, this method requires that the refractive index is independent of film thickness. In addition, it cannot be used as a routine analysis method: most often, the thin films will have to be specifically grown in two thicknesses for this analysis. A related method is based on measurements on films deposited on partly metallized substrates [19], again requiring additional care upon film deposition.

(b) Ellipsometry: this is a very powerful technique (especially spectroscopic ellipsometry) for the determination of the optical constants of thin films and substrates [20]. It has found a widespread use in the microelectronics industry [21], for the analysis of monolayer-thick oxide layers on semiconductor wafers. The strength of the technique, its extreme surface sensitivity, is its weakness at the same time: a very thin contamination layer on a thin film will yield grossly different optical constants for the film. In recent years, ellipsometric measurements have also been performed in transmission mode [22], rather than the usual reflection mode. While careful modelling of the investigated layer system for the analysis of ellipsometric measurements can certainly give good results, we will limit ourselves to spectrophotometric techniques in the rest of this paper.

2.2. Fitting of dispersion relations

A method, which is widely in use, assumes a specific—more or less empirical—dispersion equation for the wavelength-dependent complex refractive index. This method is being used in several commercial software packages for thin film optical design and analysis (TfCalc [23] and Filmwizard [24]). The equations used most often are:

(a) The Cauchy equations [25]. These equations are completely empirical and were first proposed by Cauchy (1789–1827). They are well suited to model transparent materials like SiO_2, Al_2O_3, Si_3N_4, BK7 glass, etc:

$$n(\lambda) = A_n + \frac{B_n}{\lambda^2} + \frac{C_n}{\lambda^4} + \cdots$$
$$k(\lambda) = A_k + \frac{B_k}{\lambda^2} + \frac{C_k}{\lambda^4} + \cdots$$
(1)

where wavelengths are expressed in microns. A_n, B_n, C_n, A_k, B_k and C_k are the six fitting parameters. Very often, the series

expansion is ended after the first two terms and the terms in λ^{-4} are not used.

(b) The Sellmeier relation [25, 26]. This formula was first derived by Sellmeier (1871). It is applicable to transparent materials (like the Cauchy equations) and to semiconductors (Si, Ge, GaAs, etc) in the infrared. The Sellmeier equation is a generalization of the Cauchy formulae. The original Sellmeier relation is used for completely transparent materials ($k = 0$); however, it is sometimes extended to cover the absorbing regime, using an additional formula for $k(\lambda)$:

$$n(\lambda) = \left(A_n + \frac{B_n \lambda^2}{\lambda^2 - C_n^2} \right)^{1/2}$$

$$k(\lambda) = 0 \quad \text{or} \quad k(\lambda) = \left[n(\lambda) \left(B_1 \lambda + \frac{B_2}{\lambda} + \frac{B_3}{\lambda^3} \right) \right]^{-1}$$

(2)

A_n, B_n, C_n, B_1, B_2 and B_3 are the fitting parameters in this case.

(c) The Lorentz classical oscillator model [25, 27]:

$$n^2 - k^2 = 1 + \frac{A\lambda^2}{\lambda^2 - \lambda_0^2 + g\lambda^2/(\lambda^2 - \lambda_0^2)}$$

$$2nk = \frac{A\sqrt{g}\lambda^3}{(\lambda^2 - \lambda_0^2)^2 + g\lambda^2}$$

(3)

with λ_0 the oscillator central wavelength, A the oscillator strength and g the damping factor. In the first of the two formulae, the one at the right-hand side represents the dielectric function at infinite energy (zero wavelength). For most purposes, it is more realistic to replace it by a fitting parameter ε_∞, representing the dielectric function at wavelengths much smaller than measured. The equations (3) are easily solved for n and k, but yield rather unwieldy expressions when written down explicitly.

One of the advantages of these equations over those from Cauchy and Sellmeier, is that they present a set of coupled equations for n and k, consistent with the Kramers–Kronig (KK) relations. The Forouhi–Bloomer set of equations also take this into account.

(d) The Forouhi–Bloomer dispersion relations have been developed for modelling the complex index of refraction of crystalline semiconductors and dielectrics on a rigorous basis [28–31]. The formula for $n(E)$ is deduced explicitly from $k(E)$ using the KK-relations:

$$k(E) = \sum_{i=1}^{q} \frac{A_i(E - E_g)^2}{E^2 - B_i E + C_i}$$

$$n(E) = n(\infty) + \sum_{i=1}^{q} \frac{B_{oi}E + C_{oi}}{E^2 - B_i E + C_i}$$

(4)

with

$$B_{oi} = \frac{A_i}{Q_i} \left(-\frac{B_i^2}{2} + E_g B_i - E_g^2 + C_i \right)$$

$$C_{oi} = \frac{A_i}{Q_i} \left((E_g^2 + C_i)\frac{B_i}{2} - 2E_g C_i \right)$$

$$Q_i = \tfrac{1}{2}(4C_i - B_i^2)^{1/2}$$

(5)

Not all the parameters in equations (4) are independent; dependences are defined in equations (5). Therefore, only

$n(\infty)$, A_i, B_i, C_i and E_g remain as independent fitting parameters. The equations have been implemented in a series of thin film analysis tools, using reflectance measurements and mainly focused on the semiconductor industry [32].

Remark that the Forouhi–Bloomer equations were essentially introduced to only model the interband region of materials [31], i.e. at photon energies higher than the band gap energy; however, they also have been applied in the sub-bandgap region [33]; it will be evaluated whether they can provide the same level of precision as the other dispersion equations in the region of normal dispersion of a wide bandgap material.

(e) The Drude model: for metals, the dielectric function is governed by free carriers. When ω_p is the plasma frequency ($\omega_p^2 = 4\pi ne^2/m$) and ν the electron scattering frequency, the Drude dielectric function is given by [34]:

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\nu)}$$

(6)

Usually, the parameters in the dispersion equations are determined using a least squares fitting procedure, comparing the experimental transmission spectrum against the spectrum, calculated from (n, k) and the usual equations for the transmission of an absorbing thin film, as given in appendix. In most instances, it is straightforward to include the film thickness as a fitting parameter.

Like the Forouhi–Bloomer equations, the Sellmeier and Lorentz-oscillator dispersion equations can be extended to multiple oscillators if needed [35]; for some materials, it is necessary to combine an oscillator-type dispersion relation with the Drude model.

Any of the dispersion equations can yield very good results for a large number of materials and over a quite large wavelength region. The applicability of an equation is guaranteed if there is a good fit between the experimental transmission spectrum and the one, calculated from the dispersion equations. Indeed, all of these dispersion equations are slowly varying functions of wavelength, and there is no means to obtain a good fit over a large wavelength range, using a wrong set of (n, k) data. This is due to the fact that n and k (together with the film thickness d) very directly determine the form of a transmission spectrum (also see figure 2): the spacing of the interference fringes follows from the product of the film thickness and the refractive index (the optical thickness). If the refractive index dispersion is negligible (which is usually the case well away from the absorption edge), the order of interference m at the transmission maximum at wavelength λ_1 is:

$$m = \left[\frac{\lambda_2}{\lambda_1 - \lambda_2} \right]$$

(7)

where λ_1 and λ_2 are the wavelengths of two adjacent transmission maxima ($\lambda_1 > \lambda_2$) and the symbol $[x]$ stands for nearest integer. The maximum transmittance is determined by the product of d and the extinction coefficient k, and the height of the fringes is determined in first approximation by n (from equation (A1), with $k = 0$). In this way, with a little experience, the thickness and (n, k) can often be estimated from a transmission spectrum at first sight. The transmission spectrum of figure 2 easily allows such a 'paper and pencil'

approach. In this case, the extinction coefficient k is so low, that the transmission extrema are found from (see appendix):

$$nd = \frac{m\lambda}{2}$$
$$nd = \frac{(m+1)\lambda}{4}$$
(8)

for transmission maxima and minima, respectively. The determination of the wavelengths of the transmission extrema, together with the value of the interference order (formula 7) then allows to determine the product nd at each extremum wavelength. The accurate determination of the real part of the refractive index at only one wavelength (e.g. at a point where the absorption is negligible) makes it possible to determine both the film thickness and n at each extremum wavelength. The result of this procedure in the case of the spectrum of figure 2 is also shown in table 1 and figure 3.

However, one must take care in the case of very thin or strongly absorbing films, since they show no interference fringes and fits can give multiple solutions. It is, unfortunately, not easy to quantify the error limits for the most general case of film thickness, n and k.

The dispersion relation method is very powerful and can yield very accurate data, especially for thin films (or even thin film stacks) with some known parameters (like film thicknesses or material data from previous experiments). The only limitation of the method is that one has to make assumptions about the type of dispersion relation before starting the fitting procedure.

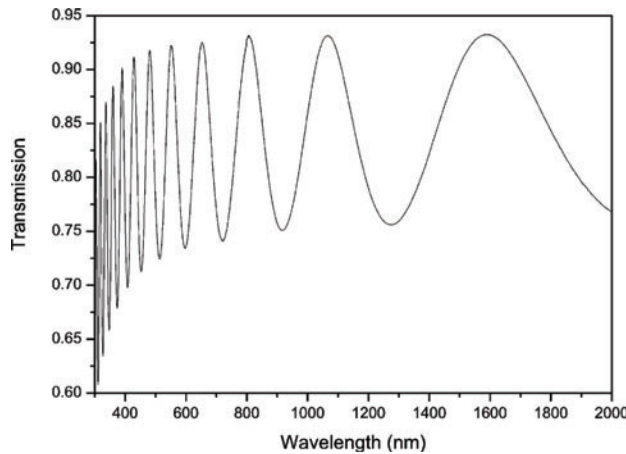More general physical constraints on the complex refractive index, not implying a specific functional relationship, have been explicitly used by Chambouleyron *et al* [36–39] for a constrained optimization approach to the extraction of n and k from transmittance data. The authors assumed the following physical constraints, usually valid for semiconductors and insulators in the region of normal dispersion:

(1) $n(\lambda) \geqslant 1$ and $k(\lambda) \geqslant 0$ for all λ.
(2) $n(\lambda)$ and $k(\lambda)$ are decreasing functions of λ.
(3) $n(\lambda)$ is convex (which translates into $n''(\lambda) \geqslant 0$).
(4) There is a infliction point λ_{infl} such that $k(\lambda)$ is convex if $\lambda \geqslant \lambda_{infl}$ and concave if $\lambda < \lambda_{infl}$.

Then, a pointwise optimization method was developed for the least squares fitting of experimental transmission spectra against the spectra, calculated from $n(\lambda)$ and $k(\lambda)$, explicitly taking into account these constraints [36]. While this method was shown to yield reliable results, it presents a serious mathematical challenge. Therefore, the method was converted into a mathematically and computationally easier unconstrained optimization [37]. This was cleverly made possible by a change to new fitting variables, automatically including the physical constraints. For example, the constrained optimization of $n(\lambda) \geqslant 1$ could be converted to the unconstrained optimization of a variable v, with $n(\lambda) = 1 + v^2(\lambda)$.

It is worth inquiring how well the previously discussed dispersion relations comply with the physical constraints set by Chambouleyron:

- The Cauchy equations comply with the first three constraints, provided all the fitting constants are positive. If the coefficient C_k is negative, the last constraint can also be fulfilled.
- The Sellmeier relation for $n(\lambda)$ is also consistent with the first three constraints, at wavelengths well above the critical wavelength C_n. For $k(\lambda)$, the constraints can all be fulfilled, dependent on the fitting coefficients.
- The Lorentz oscillator model is intrinsically consistent with the constraints, again if the wavelength is sufficiently longer than the oscillator wavelength.
- The Drude model only applies to metals, not to semiconductors or insulators in their transparent region, where they show normal dispersion and thus obviously is not consistent with the constraints.
- Since the Forouhi–Bloomer equations were introduced to describe the refractive index dispersion of materials at energies higher than the band gap, the constraints are intrinsically not fulfilled.

All the methods discussed so far, require the user to make certain assumptions about the nature of the refractive

Figure 2. Experimental transmission spectrum of an electron beam deposited SrS thin film on fused silica.

Table 1. Results of different analysis methods for single transmission spectra of a SrS thin film.

Method	Data range (nm)	Film thickness (nm)	RMS (%)	n (2000 nm)	n (500 nm)
Cauchy	300–2000	798.3	0.71	1.997	2.091
Sellmeier	300–2000	796.3	0.31	1.995	2.101
Lorentz	300–2000	793.9	0.36	2.002	2.107
Paper and pencil	N.A.	792.6	N.A.	1.994	2.114
Forouhi–Bloomer	500–2000	793.0	0.38	1.988	2.096
Swanepoel	N.A.	794.5	N.A.	1.995	2.107
Chambouleyron	300-2000	796.6	0.22	1.988	2.101

RMS: deviation between experimental data and fitted results.
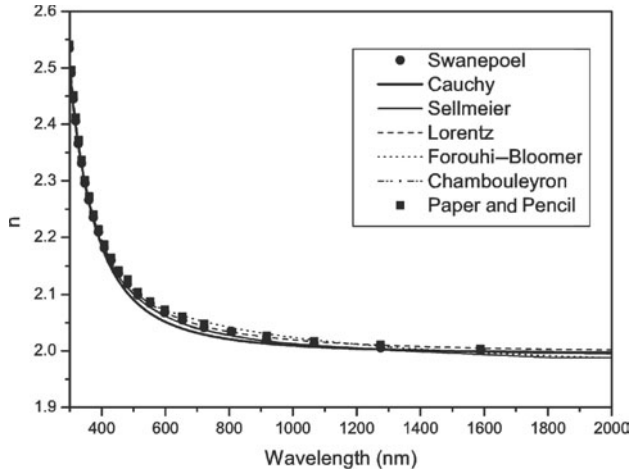
Figure 3. Real part of the wavelength-dependent refractive index, extracted from the transmission spectrum of figure 2.

index dispersion involved. This is no problem for the majority of the more common materials, but for research work, involving new or exotic materials (multiple phases, localized absorption bands, unusual band edge absorption, etc) one needs the freedom to leave any possible kind of refractive index dispersion open. Remark that the methods, based on two different measurements, do not necessitate any assumptions. In the next section, we will describe and evaluate some other assumption-free methods.

2.3. Use of 'virtual measurements'

2.3.1. Envelope method. In 1976, Manifacier *et al* [40] introduced a clever way to interpret optical transmission spectra for (n, k) extraction. This method was further developed by Swanepoel [41] and also found its way into commercial thin film software [42, 43]. The method is applicable to any transmission spectrum showing appreciable interference fringes. From the transmission spectrum, envelopes around the transmission maxima and transmission minima are constructed. Then, the envelopes around the maxima and minima are considered as continuous spectra vs wavelength, $T_M(\lambda)$ and $T_m(\lambda)$, respectively. n and k can now be calculated from T_M and T_m at each wavelength. The envelope method is highly useful and very straightforward. A few pitfalls are:

- There is no 'right' way to construct the envelopes between interference extremes. Usually, they are constructed using parabolic interpolation, but this is in fact an arbitrary choice.
- The envelopes should ideally be constructed from the tangent points touching the transmission curve, not from the interference extremes: it is easy to see that, especially in a region where the transmission is changing fast, connecting the extremes will yield $T_M(\lambda)$ and $T_m(\lambda)$ curves that are actually too close to each other. More recently, efforts have been undertaken to increase the accuracy of the envelope determination [44, 45].
- The method cannot cope with local absorption features if the film is not very thick, i.e. if the absorption bands fall in between interference extremes.

- The accuracy of the method decreases with decreasing film thickness, since at lower film thickness, the interference extremes are spaced further apart and interpolation between these extremes becomes more difficult.
- The method fails if the absorption in the film is so high that interference fringes are not visible and $T_M(\lambda)$ and $T_m(\lambda)$ curves coincide. In its original form [41], the method then reduces to a Cauchy dispersion relation fit.

When carefully implemented, the envelop method is applicable as a routine analysis technique. Some efforts have been undertaken to evaluate the method's accuracy [46] and to refine the method to avoid multiple solutions [45, 47]. Recently, the effect of substrate absorption has been incorporated in the method [48].

2.3.2. KK analysis of transmittance data. Following the KK relations, the transmission of a material and the phase shift upon transmission are related by [49]:

$$\varphi(\lambda_0) = \frac{2\lambda_0}{\pi} P \int_0^{+\infty} \frac{\ln t_f(\lambda)}{\lambda_0^2 - \lambda^2} \, d\lambda - \frac{2\pi d}{\lambda_0} \tag{9}$$

with P the Cauchy principal value of the integral and t_f the internal transmission of the film. This equation implies that, given the transmission of any material at all wavelengths (clearly an impossible experiment), the corresponding phase shift can be calculated. The transmission and the phase shift could then be used as two independent variables, enabling the calculation of n and k of the material at any wavelength. In order to calculate the above integral, Nilsson [9] introduced the following extrapolation procedure. Using the mean-value theorem, one can write:

$$\varphi(\lambda_0) = A(\lambda_0) \ln \left| \frac{\lambda_L + \lambda_0}{\lambda_L - \lambda_0} \right| + \frac{2\lambda_0}{\pi} P \int_{\lambda_L}^{\lambda_H} \frac{\ln t_f(\lambda)}{\lambda_0^2 - \lambda^2} \, d\lambda$$
$$+ B(\lambda_0) \ln \left| \frac{\lambda_H + \lambda_0}{\lambda_H - \lambda_0} \right| - \frac{2\pi d}{\lambda_0} \tag{10}$$

where λ_L and λ_H are the lower and upper wavelength limits of the measurement range. As an approximation, A and B are then assumed to be constant [50, 51]. If the complex refractive index of the film is known for two well-separated wavelengths, the corresponding phase shift can be calculated and, from the above integral, A and B can be determined. The singularity in the integral can be removed by subtracting some part from the integral and adding it back in its integrated form [49]:

$$P \int_{\lambda_L}^{\lambda_H} \frac{\ln t_f(\lambda)}{\lambda_0^2 - \lambda^2} \, d\lambda = \int_{\lambda_L}^{\lambda_H} \frac{\ln t_f(\lambda) - \ln t_f(\lambda_0)}{\lambda_0^2 - \lambda^2} \, d\lambda$$
$$- \frac{1}{2\lambda_0} \ln t_f(\lambda_0) \ln \left| \frac{(\lambda_0 + \lambda_L)(\lambda_H - \lambda_0)}{(\lambda_0 - \lambda_L)(\lambda_H + \lambda_0)} \right| \tag{11}$$

While using the KK relations for the analysis of transmission spectra is theoretically very elegant (it does not need any *a priori* assumptions regarding the refractive index dispersion), it is quite difficult to implement as a tool for routine analysis:

- With the equations given, one needs the separate determination of (n, k) at two distinct wavelengths.

- Near the ends of the measurement interval [λ_L, λ_H], the error due to the approximation of A and B being constant, gets quite large. It is not easy to evaluate this error in the most general case. Consequently, the transmission should be measured over the maximum possible wavelength range.
- The calculation of (n, k) from (T, φ) requires a numerical iteration procedure, which can—in the worst case—converge to an erroneous solution.

In 1998, Palmer *et al* [52] described a new, multiply subtractive KK method for the evaluation of infrared optical data. While this technique seems quite promising, it also requires the independent determination of (n, k) at certain wavelengths; in addition, it is not clear what accuracy can be obtained for data in the ultraviolet–visible (UV–VIS) region, where the transmission usually becomes extremely low at the UV-side, due to band edge absorption.

3. Critical evaluation

In order to get more feeling for the similarities and the differences of the different analysis methods, several of these were applied to the transmission spectrum of a real thin film. Only the following methods, using a single transmission spectrum and thus fit for routine analysis, were selected:

- Fitting of dispersion relations:
  * Cauchy equations,
  * Sellmeier relations (with exponential extinction coefficient),
  * Lorentz oscillator (single oscillator),
  * Forouhi–Bloomer equations (single term).
- The pointwise unconstrained optimization method of Chambouleyron *et al*.
- Swanepoel's envelope method.
- The manual 'paper and pencil' method of refractive index and thickness determination, based on positions of interference extrema.

The experimental transmission spectrum of an electron beam deposited thin film SrS on a 1 mm thick fused silica substrate was used [53]. SrS is a wide band gap semiconductor ($E_g \sim 4.3$ eV) with a refractive index of about 2.0; a film thickness of about 800 nm was chosen. A transmission spectrum was acquired from 250 to 2000 nm, using a Varian Cary 500 spectrophotometer. An almost ideal 'textbook' transmission spectrum was obtained (figure 2), showing no signs of film or thickness inhomogeneities or scattering.

The transmission spectrum was used at 1 nm intervals, and first corrected for the (small) absorption in the fused silica substrate. Fitting of the dispersion relations was performed using the solver function in Microsoft Excel. The software for the unconstrained optimization was provided by the research group of Chambouleyron. The commercial software package Essential McLeod [42] was used for the Swanepoel method.

Table 1 summarizes some of the results of the different analysis methods. The most important figure of merit for the fitting method is the root mean square (RMS) deviation between the experimental transmission spectrum and the spectrum, obtained from the modelled refractive index

dispersion. The deviations in table 1 are hardly influenced by the experimental errors: the noise level of the experimental transmission spectrum amounted to only 0.02% (RMS).

The Sellmeier, Lorentz and Forouhi–Bloomer equations used only a single term in the dispersion equation, resulting in six, four and five fitting parameters, respectively, (not taking into account the film thickness). The Cauchy equations also contain six fitting parameters. The actual n and k dispersion, as determined by the five different methods, is shown in figures 3 and 4. Based on these figures and the data from table 1, the following conclusions can be drawn:

- The Cauchy equations do not yield an optimum result, yielding a rather large RMS deviation of 0.71% while still using six parameters. Since these equations are the only ones that are fully empirical, this does not come as a surprise.
- The Sellmeier relations yield a remarkably good result for the present type of material. We obtained similar good results on tellurides earlier [49]. The Sellmeier relations are semi-empirical in the sense that they are a simplification of the Lorentz classical oscillator model.
- The classical oscillator model also gives very good results: a very large wavelength range is covered with only four fitting parameters.
- Using only a single term in the dispersion equations, the Forouhi–Bloomer model did not yield good results for the 300–2000 nm range. Only for a smaller range, decent results, comparable with the other dispersion relations, were obtained. While the single-term version of this model is apparently not suitable for the present data set, the Forouhi–Bloomer equations are ideally fit for the analysis of optical spectra covering several absorption bands, e.g. at photon energies above the fundamental energy gap [31], where the standard dispersion relations fail.
- The envelope method (often named after Swanepoel) gives very much the same results as the other methods, but evidently only yields refractive index values at the wavelengths corresponding to the extremes of the interference fringes.
- The 'paper and pencil' method works very well for the present kind of near ideal transmission spectrum. Just
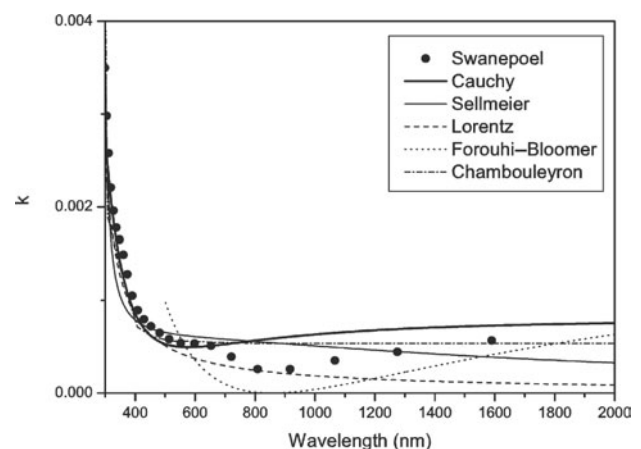

Figure 4. Imaginary part of the wavelength-dependent refractive index, extracted from the transmission spectrum of figure 2.

like the Swanepoel method, it is only applicable when well resolved interference extrema are visible. The extinction coefficient k was not calculated using this method, since it intrinsically yields the same result as the Swanepoel method.

- The method due to Chambouleyron has to be considered as a generalization of the methods using dispersion relations, requiring only the assumption of very general physical constraints. Just as the dispersion relation methods, it can also be used in the case of much thinner films, where hardly any interference effects can be seen. For the present transmission spectrum, it yields results, perfectly comparable to those of the other methods.
- For the functional behaviour of $k(\lambda)$ (figure 4), a monotonously decreasing function is expected (this is also an explicit physical constrain set by Chambouleyron). The Cauchy and Forouhi–Bloomer dispersion relations are not acceptable from this point of view. Also the Swanepoel method yields a non-monotonous function, but remark that for the present transmission spectrum, the absorption is so low, that minute differences in optical transmission yield very large relative differences in extinction coefficient.
- The standard deviation of the film thickness and refractive index values of all tested methods is of the order of 0.25%, which has to be considered as an error estimate for these methods.
- As seen from figures 3 and 4, all methods are able to reproduce the same kind of dispersion behaviour for n, the real part of the refractive index. There is some scatter of the values of k, the imaginary part, but this is mainly due to the very low extinction coefficient, combined with a relatively small film thickness; therefore, the seemingly large relative differences in k are responsible for only very small changes in transmission. The dispersion of k is not that well reproduced by the Forouhi–Bloomer set of equations. Remark that the Forouhi–Bloomer equations (formula (4)) imply that the extinction coefficient turns zero at the energy gap E_g, and increases both below and above E_g. The SrS film studied at sub-bandgap energies follows the usual behaviour, having almost zero absorption at long wavelengths and showing a slowly increasing absorption towards the band gap. This is clearly not consistent with the single-term Forouhi–Bloomer model.

4. Conclusions

A general overview has been given of the methods that can be used for the routine determination of the wavelength dependent complex refractive index of thin films, using simple spectrophotometric equipment. Of all the methods presented, those using only one normal incidence transmission spectrum are clearly the easiest to apply. If the thin film:

(1) shows no very localized absorption bands (in between interference extremes),
(2) shows low enough absorption so that interference fringes are visible,
(3) has an optical thickness high enough to yield a few interference extremes in the transmission spectrum (this typically means an optical thickness larger than about 400 nm for visible and near infrared spectra)

then the envelope method or the paper and pencil approach are by far the easiest methods to apply; a clear advantage of the methods is that no dispersion equation has to be chosen and no parameters have to be introduced.

If the above conditions (2) or (3) are not fulfilled, fitting to one of the dispersion relations or application of the Chambouleyron method is still possible. For the type of material (SrS, a wide band gap semiconductor) and the wavelength region (well above the band gap cut-off) shown in this paper, the Sellmeier and classical oscillator models are the best choices, the latter having the advantage of incorporating the lowest number of fitting parameters; moreover, these methods are computationally much simpler than the Chambouleyron method. If condition (1) is not fulfilled, and there are local absorption bands, a multiple oscillator fitting approach seems the most appropriate. While the Cauchy equations are probably never the best choice, the Forouhi–Bloomer equations should yield good results for extended wavelength ranges, covering several absorption bands.

Appendix

For a system of an absorbing plane parallel thin film on a non-absorbing substrate, the optical transmission T for normal incidence is given by the following equations, as written in a quite elegant form by Swanepoel [41]:

$$T = \frac{Ax}{B - Cx + Dx^2} \qquad (A1)$$

where

$$A = 16n_s(n^2 + k^2)$$

$$B = [(n+1)^2 + k^2][(n+1)(n+n_s^2) + k^2]$$

$$C = [(n^2 - 1 + k^2)(n^2 - n_s^2 + k^2) - 2k^2(n_s^2 + 1)]2\cos\varphi$$

$$-k[2(n^2 - n_s^2 + k^2) + (n_s^2 + 1)(n^2 - 1 + k^2)]2\sin\varphi$$

$$D = [(n-1)^2 + k^2][(n-1)(n - n_s^2) + k^2] \qquad (A2)$$

$$\varphi = \frac{4\pi nd}{\lambda}$$

$$x = \exp(-\alpha d)$$

$$\alpha = \frac{4\pi k}{\lambda}$$

n and k are the real and imaginary parts of the thin film refractive index, d is the film thickness and n_s is the (real) substrate refractive index. Multiple reflections inside the substrate are taken into account, but these are assumed to be incoherent (i.e. the substrate is sufficiently thick so that it does not give rise to additional interference effects).

Acknowledgments

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