Determination of optical constants of thin film coating materials based on inverse synthesis

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A versatile method for determination of the optical constants is described that can be applied to a variety of coating materials. It is based on the use of an optical thin film synthesis program to adjust the constants of dispersion equations until a good fit is obtained between measured and calculated spectral transmittance and/or reflectance curves. The sensitivity of the determination can be increased by a suitable combination of measurement quantities. Because more than the minimum amount of data can be used, sensitivity to measurement errors and the chances of obtaining multiple solutions can both be reduced. To illustrate the method optical constants are determined of MgF_2, ZnS, MgO, Inconel, and Si films in the visible part of the spectrum and of ITO films in the 0.4–12.0-μm range.

I. Introduction

It is important during the design of an optical multilayer interference system that the optical constants of all the materials used in it be known. If the chosen deposition process results in porous films, the optical constants of the film will differ from those of the bulk material. In such cases it is often necessary to know for design purposes the aged optical constants of the films after their exposure to the atmosphere as well as their vacuum values for the optical monitoring of the thicknesses of the individual films during their deposition. It is a fact that even for the same deposition equipment the optical constants of the resulting films may vary with the process parameters. Clearly, therefore, a need exists for a convenient method to determine the optical constants from relatively simple measurements made on an easy to use commercial apparatus. The accuracy of the determination should be better than the repeatability of the constants from one production run to another.

In this paper some basic properties of the main approaches to the determination of the optical constants of coating materials are discussed (Sec. II). Our inverse synthesis approach to this problem is based on the use of a computer program for the numerical design of multilayer interference coatings (Secs. II and III). In it the refractive index n and absorption coefficient k are found by adjusting the constants of dispersion equations (Sec. IV) until a good fit between the measurements and

calculations is obtained. A brief description of the experimental conditions (Sec. V) and of the results of measurements on a number of different coating materials (Sec. V) is also given.

II. General Discussion of Methods for Determination of Optical Constants of Thin Films

In the past many papers have been published on the determination of the optical constants of thin films. A thorough evaluation of this vast body of work is outside the scope of this article, and the interested reader is referred to existing reviews.[1-3] Nevertheless, for a proper discussion of our work it is necessary to mention the basic properties of the existing methods. For this purpose it is convenient to classify them into single- and multiwavelength determinations.

A. Single-Wavelength Methods

The main single-wavelength methods for determination of n and k are based on photometric, ellipsometric, or interferometric measurements. As a rule no relationship between n and k is assumed. Frequently, the thickness t of the thin film is determined simultaneously. The number of independent measurements equals the number of unknowns. Typical quantities that are measured include transmittance, the phase change on transmission, reflectance or phase change on reflection for radiation incident from the medium or substrate side, and the phase differences between parallel and perpendicularly polarized reflected or transmitted beams. The measurements may be made at normal or oblique angles for radiation polarized parallel or perpendicular to the plane of incidence.

Various combinations of measurement quantities have been investigated for a range of values of n, k, and

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t for both normal[4] and oblique[5-10] angles of incidence. Combinations have been found that yield the best sensitivity for a given combination of n, k, and t values. Single-wavelength determinations are, therefore, capable of accurate results but only for careful measurements on custom-built equipment.[11-13] Both random and systematic errors in the measurements have serious effects on the results.

A further problem arises from the fact that the expressions relating the construction parameters to the measurement quantities are very complex. Explicit expressions for n and k cannot, in general, therefore, be derived, and the constants have to be determined from nomograms or by successive refinement of suitable starting values. This latter approach often leads to multiple solutions, and the result depends on the starting values chosen. Furthermore, slight experimental errors can cause convergence to wrong solutions or prevent a solution from being obtained at all. In some methods these problems are avoided by the use of additional measurements in the determination or by the selection from all the possible solutions of those sets of n and k which yield a reasonable progression of values over an extended spectral region.[14,15]

B. Multiwavelength Methods

The main multiwavelength methods for determination of the optical constants of thin films are based on the Kramers-Kronig relation or on curve fitting with the aid of dispersion equations. The values of n and k obtained in this way are interdependent, and this limits the number of solutions. The fact that transmittance and/or reflectance is measured (at normal incidence) over an extended spectral region also reduces the likelihood of multiple solutions. In all the work we are aware of, the substrate carries a single film whose thickness is frequently also determined. Some multiwavelength methods are relatively insensitive to random measurement errors.

The Kramers-Kronig methods require that the reflectance or transmittance of the substrate–film combination be known for all wavelengths. This then permits the phase change to be calculated as a function of wavelength. The optical constants are then found by successive approximations from the rather complicated expressions for the transmittance[16-18] or reflectance[19,20] of a single film. However, in practice measurements are not available for all wavelengths, and so corrections have to be applied. These can introduce uncertainties in n and k in the neighborhood of the two wavelength limits of the measurements.

In the multiwavelength curve fitting methods the dispersion of the optical constants is represented by dispersion equations. These can be based on theoretical considerations (interband transition model,[21] free electron gas model, or a combination of the two[22,23]) or on analytical formulas (Sellmeier,[24,25] Cauchy[26]). In the former case causality conditions are satisfied. The initial estimates of the constants of these equations are then gradually adjusted until a fit between the experimental measurements and the values calculated from the thin film formula is obtained. The advantage of this approach is that the measurements (and the fit) need not extend beyond the spectral range of interest. However, the assumption that the dispersion of the optical constants can be adequately represented by such simple models is not always justified.

C. Present Method

The method described in this paper clearly falls into the category of multiwavelength curve fitting methods. However, it is based on a powerful computer program that has been originally developed for the design of optical multilayer coatings. This makes it possible to incorporate the positive features and avoid some of the limitations of the other methods. For example, the sensitivity of the determination of n and k can be increased by (a) choosing an optimum combination of measurement quantities, (b) selecting sensitive angles of incidence, and (c) incorporating films of the unknown material in specially selected multilayers.

If the more convenient, although less accurate, commercial spectrophotometers are to be used for the measurements, the sensitivity of the determination to measurement errors should be reduced. This can be done by finding the rms fit to more than the minimum required amount of data. Additional measurements might include the spectral transmittance and/or reflectance (a) at two or more angles of incidence for one or both planes of polarization, (b) of a film in air and with a cover glass attached to it with a suitable contact liquid,[27] (c) of a film deposited over two different known thin film systems, (d) of two or more thicknesses of the unknown material, and (e) of several different multilayers containing the unknown material.

A by-product of the use of such additional measurements is that, with their careful choice, the chances of obtaining multiple solutions can be reduced to zero.

More details of this method will be given in the following sections.

III. Computer Program

A detailed description of the program FILTER used for determination of the optical constants will be found in Ref. 28. Here brief mention will be made only of those of its features that are necessary for understanding the method.

Among other quantities, the program calculates for any wavelength λ, angle of incidence θ, and plane of polarization of the incident radiation the transmittance T and reflectances R and R' for radiation incident from either medium of an optical multilayer interference coating consisting of l dielectric, semiconducting, or metallic layers (Fig. 1). The program assumes that the layers are homogeneous and that there are no surface absorption effects.[29] Each of these layers can, therefore, be characterized by its metric thickness t_i, refractive index n_i, and absorption coefficient k_i. n and k can be calculated for any wavelength from the constants $A, B, C, \ldots$, of a set of dispersion equations (see Sec. IV).
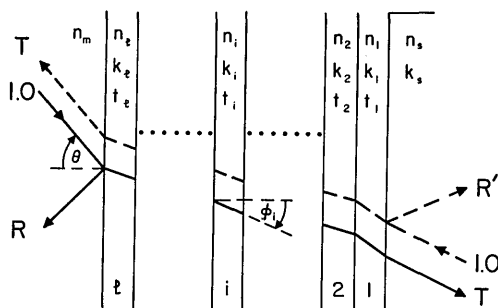
Fig. 1. Thin film terminology.

When the program is used to determine the construction parameters of a multilayer system, a single-valued merit function M is defined in terms of the differences between the calculated C and experimentally measured E values of any desired combination of m photometric quantities T, R, and R':

$$M = \left\{ \frac{1}{m} \sum_{i=1}^{m} \left(\frac{C_i - E_i}{\varepsilon_i} \right)^2 \right\}^{1/2}, \tag{1}$$

where ε_i is the accuracy with which the ith photometric quantity can be measured. (This normalization is important for a balanced solution of the data.) Clearly the merit function depends on the construction parameters of the layer system

$$M = M[n_s, k_s, n_m, (n_i, k_i, t_i), i = 1, 2, \ldots, l] \tag{2}$$

and where

$$n_i = n_i(A_i, B_i, C_i, \ldots),$$
$$k_i = k_i(A_i, B_i, C_i, \ldots). \tag{3}$$

To find the unknown construction parameters t_i, n_i, and k_i of a multilayer system, the initial values of $A_i, B_i, C_i, \ldots$, are gradually refined until a minimum value of the merit function is achieved. The final values of $A_i, B_i, C_i, \ldots$, will yield the correct values of n_i and k_i if the fit between the calculated and experimental values is good and providing that an adequate definition of the merit function has been chosen so that physically meaningless solutions are avoided.

In the above form the method has been used successfully at the NRCC for many years. However, a more recent modification of the program[28] makes the method even more powerful. It is now possible to define a merit function in terms of the calculated and measured performances of several different systems that are made of the same materials:

$$M = \left\{ \frac{1}{m_1 + m_2 + \ldots m_j} \left[\sum_{i=1}^{m_1} \left(\frac{C_{1,i} - E_{1,i}}{\varepsilon_{1,i}} \right)^2 \right. \right.$$
$$\left. \left. + \sum_{i=1}^{m_2} \left(\frac{C_{2,i} - E_{2,i}}{\varepsilon_{2,i}} \right)^2 + \ldots \right] \right\}^{1/2}. \tag{4}$$

As mentioned before, a suitable choice of thin film systems greatly reduces the chances of finding a physically meaningless set of optical constants.

IV. Dispersion Equations

The dispersion of the optical constants of materials has been the subject of many intensive theoretical investigations.[30,31] These have not yet resulted in adequate explanations of the optical constants of all materials. Nevertheless, for many years we have found it convenient to describe the dispersion of the optical constants in our computer programs by means of dispersion equations. Presently we can evaluate n and k from equations based on the following models.

(a) The interband transition (Lorentzian) model, useful for the optical constants of dielectric materials:

$$n^2(\lambda) = A + k^2(\lambda) + \sum_{i=1}^{J} \frac{B_i \lambda^2(\lambda^2 - C_i^2)}{(\lambda^2 - C_i^2)^2 + D_i^2 \lambda^2}$$

$$k(\lambda) = \frac{1}{2n(\lambda)} \sum_{i=1}^{J} \frac{B_i D_i \lambda^3}{(\lambda^2 - C_i^2)^2 + D_i^2 \lambda^2}, \tag{5}$$

where A is the low wavelength contribution to the refractive index and B_i, C_i, and D_i are related to the strength, resonance wavelength, and linewidth, respectively, of the ith of the J different dipoles used to describe the material.

(b) The free electrron gas (Drude) model, useful for some metals:

$$n^2(\lambda) = A + k^2(\lambda) + \frac{B\lambda^2}{(1 + C^2\lambda^2)} \, ,$$

$$k(\lambda) = \frac{BC\lambda^3}{2n(\lambda)(1 + C^2\lambda^2)} \, , \qquad (6)$$

where, according to theory, A is unity and B and C are proportional to the product of the oscillator strength and the square of the plasma frequency and to the inverse of the relaxation time of the electrons in the conduction band.

(c) A combination of the Lorentzian and Drude models:

$$n^2(\lambda) = A + k^2(\lambda) + \frac{B\lambda^2}{(1 + C^2\lambda^2)} + \sum_{i=1}^{J} \frac{B_i\lambda^2(\lambda^2 - C_i^2)}{(\lambda^2 - C_i^2)^2 + D_i^2\lambda^2} \, ,$$

$$k(\lambda) = \frac{1}{2n(\lambda)} \frac{BC\lambda^3}{(1 + C^2\lambda^2)} + \sum_{i=1}^{J} \frac{B_iD_i\lambda^3}{(\lambda^2 - C_i^2)^2 + D_i^2\lambda^2} \, . \qquad (7)$$

(d) Simplified Sellmeier equations:

$$n^2(\lambda) = 1.0 + \frac{A}{1.0 + (B/\lambda)^2} \, ,$$

$$k(\lambda) = \frac{C}{n(\lambda)D\lambda + \dfrac{E}{\lambda} + \dfrac{1}{\lambda^3}} \, , \qquad (8)$$

which are valid only in spectral regions away from the absorption band, and in which n and k are not calculated from the same constants.

Theories used to derive Eqs. (5)–(7) yield theoretical values for the constants $A, B, C, \ldots$, for a given material. In practice, experimental results are better represented with constants that have been obtained empirically. We follow this approach in our computer program since we use the dispersion equations only as a convenient vehicle to describe the variation in n and k required to fit the experimental results and since we are not interested in ascribing any physical meaning to the actual values of $A, B, C, \ldots$.

A limitation of this approach is that the general form of the above equations is not quite suitable to describe adequately the optical constants of some materials over an extended spectral region. This is especially true for some metals.[31] We overcome this problem by using more than one term in the Lorentzian equations or the same equation but with different constants to calculate n and k for different narrower spectral regions. Of course, when carried to the extreme, this latter procedure results in the loss of all the advantages of multi-wavelength determinations.

V. Preparation and Measurement of the Samples

Typical equipment used for the preparation of the sample coatings consisted of a Balzers BA 500 evaporation plant with a 50-cm stainless steel bell jar. A Sloan PAK-8 electron beam gun with a water-cooled rotating turret with four 30-cc capacity hearths was used to evaporate the coating materials. A 6-kV power supply provided up to 800 mA of current. An x-y sweep could be applied to the electron beam, and its diameter could be adjusted. In all cases the films were deposited onto 5- $\times$ 5-cm glass or quartz substrates that were

subjected to normal cleaning procedures prior to being discharge cleaned and heated to 150°C in the vacuum. Deposition took place normally at a rate of ~15 Å/sec and at a pressure of the order of 10^{-5} Torr. The exception to this were ZrO_2 films which were deposited by reactive evaporation in a partial pressure of oxygen of 10^{-4} Torr. We found that films formed in this way were more homogeneous than films deposited directly from the oxide. Evidence for this was that in single films produced by the two methods at the halfwave points the departure of the reflectance from that of the uncoated substrate did not exceed ±0.5%, ±2%, respectively.

A Perkin-Elmer 330 double-beam spectrophotometer was used to make transmittance measurements in the 0.186–2.5-μm wavelength range of samples inclined to the incident beam at angles up to 60°. For relative reflectance measurements at an angle of incidence of 8°, commercial reflectance attachments could be inserted into the two sample compartments. Sheet polarizers were used for measurements at oblique angles of incidence.

Transmittance measurements in the 2.5–50-μm spectral region were made on a Perkin-Elmer 283-B spectrophotometer for angles of incidence up to 60°. A reflectance attachment permitted measurements at angles of incidence between 30 and 50°. A pair of wire grid polarizers defined the plane of polarization.

Limitations of spectrophotometers of the above type were discussed at length by Bennett and Bennett[32] in their comprehensive review article on thin film measurements. In our experiments we used microscope glass slides whenever possible. They are fire-polished and, therefore, do not introduce excessive scatter. Since our computer programs can correct for second surface reflections within the substrate when calculating transmittance and reflectance, we did not place an uncoated substrate in the reference beam. The microscope slides are thin and, therefore, do not introduce defocusing errors that are large compared with the overall accuracy of the instruments.

We use two reference standards for reflectance measurements. The first consists of a quartz plate whose reflectance is calculated from published refractive-index data. The second surface of this plate is not parallel to the first and is roughened and painted with black paint. Our second reflectance standard is a broadband all-dielectric reflector consisting of a number of contiguous quarterwave stacks made of ZrO_2 and SiO_2. Care was taken during its deposition to minimize absorption within the layers. The second surface of this plate is also roughened and painted black. The reflectance of this device was checked on a single-beam reflectometer. Throughout the visible part of the spectrum it exceeds 97%, except for a few narrow regions where it dips by a few percent. Measurements are corrected for this departure from unity.

The thicknesses of metal films were measured to ±10 Å with a Sloan Dektek I stylus instrument. During the deposition of the films a razor blade was placed against the substrate to provide a sharp edge for the measurement.

Table I. Dispersion Equation Constants for Various Materials

Material	A	B	C	B1	C1	D1	B2	C2	D2
ZnS	4.81			0.509	0.333	0.00389			
MgF_2	1.77			0.162	0.236	0.00256			
MgO	2.36			0.318	0.258	0.00320			
ZrO_2	3.42			0.272	0.299	0.00001			
Si	6.31			2.50	0.374	0.163			
Inconel*	−1.15	15.3	1.14	1.98	0.430	0.149	8.02	0.630	0.413
Inconel (t=0.0051 µm)	−4.95	19.8	1.07	1.86	0.219	0.124	5.83	0.478	0.563
Inconel (t=0.0099 µm)	−1.12	15.3	1.12	1.97	0.430	0.149	8.01	0.630	0.413
Inconel (t=0.0191 µm)	−1.61	21.4	1.54	2.16	0.435	0.154	8.55	0.631	0.348
Inconel**	0.104	0.631	1.19	−1.50	0.412	0.162	7.07	0.749	0.521

* Average values for films of calculated metric thicknesses
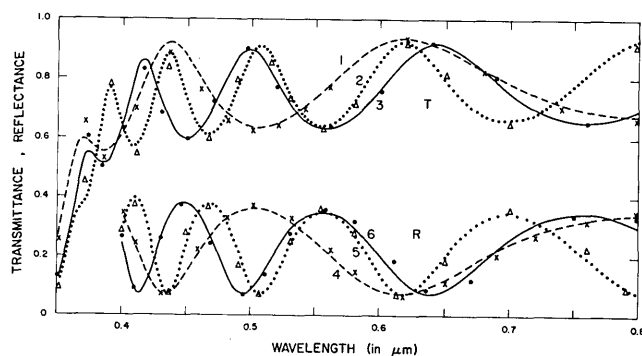** Average values for films of calculated metric thicknesses

Fig. 2.   Spectral transmittances and reflectances of three ZnS films of different metric thicknesses (0.528,0.413,0.264 µm) deposited simultaneously onto quartz substrates.

Table II. Optical Constants for Various Materials

λ (μm)	ZnS n	ZnS k	MgF$_2$ n	MgF$_2$ k	MgO n	MgO k	ZrO$_2$ n	ZrO$_2$ k	Si n	Si k
0.40	2.54_3	0.0103	1.42_1	0.0008	1.70_3	0.0022	2.00_8	0.0000	2.98_8	0.933
0.45	2.43_6	0.0044	1.41_2	0.0006	1.68_3	0.0015	1.97_6	0.0000	3.16_9	0.629
0.50	2.39_3	0.0027	1.40_7	0.0005	1.67_0	0.0011	1.96_0	0.0000	3.18_5	0.424
0.55	2.36_9	0.0019	1.40_3	0.0004	1.66_3	0.0009	1.95_0	0.0000	3.15_6	0.311
0.60	2.35_5	0.0015	1.40_1	0.0003	1.65_7	0.0008	1.94_4	0.0000	3.12_6	0.242
0.65	2.34_5	0.0012	1.39_9	0.0003	1.65_4	0.0007	1.94_0	0.0000	3.10_1	0.197
0.70	2.33_8	0.0010	1.39_7	0.0003	1.65_1	0.0006	1.93_7	0.0000	3.08_1	0.167
0.75	2.33_3	0.0009	1.39_6	0.0002	1.64_9	0.0005	1.93_4	0.0000	3.06_6	0.145
0.80	2.32_9	0.0008	1.39_6	0.0002	1.64_7	0.0005	1.93_2	0.0000	3.05_2	0.128

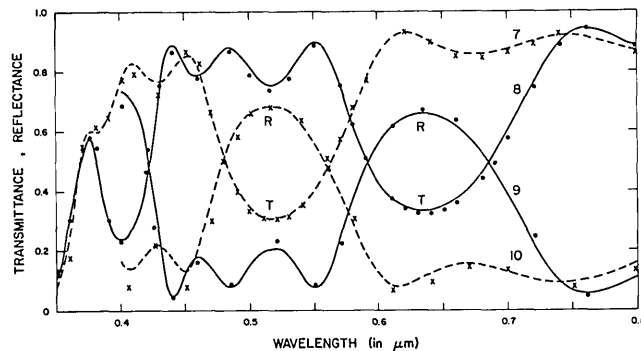| λ (μm)	Inconel* n	Inconel* k	Inconel (t=0.0051 μm) n	Inconel (t=0.0051 μm) k	Inconel (t=0.0099 μm) n	Inconel (t=0.0099 μm) k	Inconel (t=0.0191 μm) n	Inconel (t=0.0191 μm) k	Inconel** n	Inconel** k
0.40	1.51_3	2.64_3	1.55_4	1.90_5	1.51_8	2.62_3	1.53_1	2.81_2	1.33_2	1.81_1
0.45	2.18_7	2.53_0	1.86_3	1.84_8	2.18_3	2.50_9	2.21_9	2.79_7	1.14_3	2.33_9
0.50	2.48_6	2.39_3	2.16_4	1.81_5	2.47_9	2.37_9	2.56_3	2.73_5	1.02_1	2.54_6
0.55	2.79_0	2.43_8	2.43_4	1.75_8	2.78_4	2.42_8	2.93_5	2.85_8	1.09_2	2.65_0
0.60	3.18_8	2.45_0	2.67_1	1.70_8	3.18_4	2.44_4	3.44_8	2.90_4	1.29_3	2.71_4
0.65	3.57_7	2.35_2	2.87_4	1.67_3	3.57_6	2.34_8	3.94_1	2.76_0	1.57_4	2.72_5
0.70	3.87_6	2.18_3	3.05_0	1.65_2	3.87_9	2.18_1	4.28_0	2.50_4	1.88_5	2.66_0
0.75	4.07_7	2.00_6	3.20_5	1.65_0	4.08_3	2.00_4	4.46_3	2.25_1	2.17_6	2.51_8
0.80	4.20_3	1.85_7	3.34_4	1.66_1	4.21_2	1.85_5	4.54_7	2.05_7	2.41_1	2.32_3

Fig. 3. Spectral transmittance and reflectance curves of two 3-layer ZnS/MgF$_2$/ZnS systems. The metric thicknesses of the layers in order of deposition on the quartz substrate are 0.205,0.353,0.198 μm and 0.163,0.285,0.161 μm, respectively.
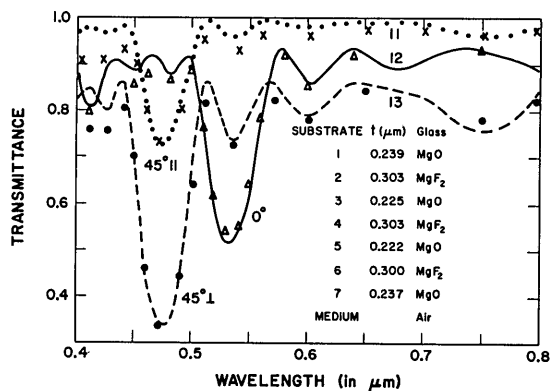
Fig. 4. Spectral transmittance curves of a 7-layer MgO/MgF$_2$ system measured at two angles of incidence.

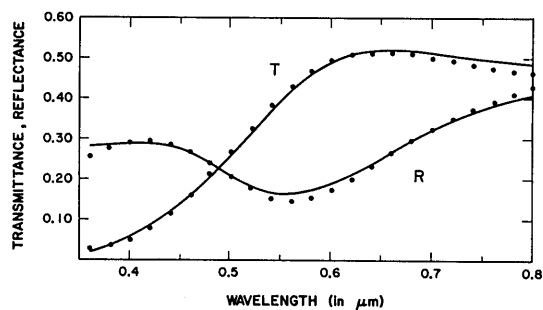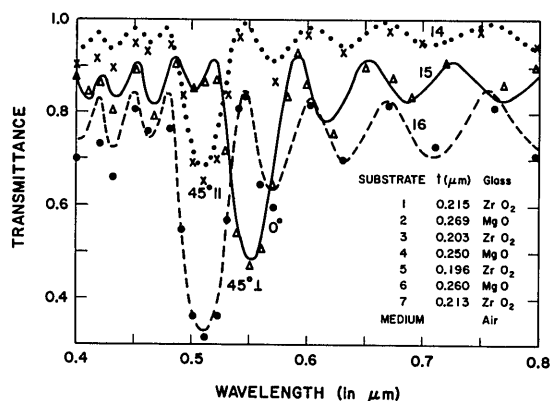Fig. 7. Spectral transmittance and reflectance curves of a silicon film on a glass substrate.

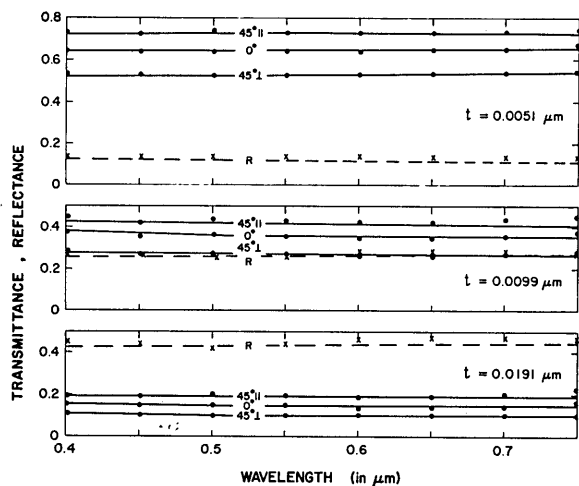Fig. 5. Spectral transmittance curves of a 7-layer ZrO$_2$/MgO system measured at two angles of incidence.

Fig. 6. Spectral transmittance and reflectance curves of three Inconel films of different thickness measured at two angles of incidence.
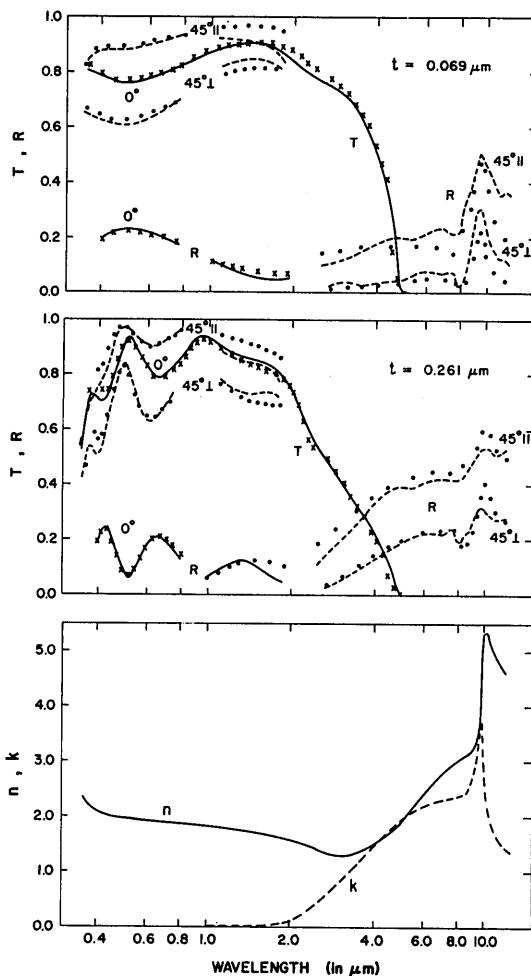

Fig. 8. Spectral transmittance and reflectance curves of two ITO films of different metric thicknesses measured at two angles of incidence and the resulting optical constants.

When used in the construction parameter determination mode, the program FILTER requires two data sets for the processing. The first contains, among other things, measured transmittances and/or reflectances that define the merit function, the measurement errors ε_i (assumed to be 0.005 and 0.01 for measurements at normal and oblique angles of incidence), as well as the nominal thicknesses of the films of the layer systems used in the determination. The second data set contains the dispersion equation constants of the known materials and the starting values of those for the material under investigation. We find the procedures described by Vierne[33] helpful in making first estimates of these constants.

The data processing can be divided into two distinct phases. In the first only the dispersion equation constants of the unknown material are varied. The values found in this first run are entered into the dispersion data set, and in the second phase calculations they are varied again along with the thicknesses of all the layers to reduce the merit function still further. The dispersion equation constants resulting from this second run yield the optical constants of the material investigated, unless any of the thicknesses were drastically changed. This would be an indication that the process converged toward a physically meaningless solution. In such a case a new determination is attempted with additional experimental data.

VI. Examples

To illustrate the method presented in this paper, we used some of the combinations of different measurements mentioned in Sec. II.C in the determination of the optical constants of diverse types of thin film coating material.

The results of these determinations are represented in Tables I and II in the form of dispersion equation constants and by values of n and k for selected wavelengths, respectively. The curves of Figs. 2–8 represent the experimental transmittances and reflectances of the layer systems used in the determinations. Calculated data are represented by points, crosses, and triangles.

A. Dielectric Films

The optical constants of a slightly absorbing, high refractive-index material can be obtained, for example, from normal incidence spectral transmittance and reflectance measurements on a film whose thickness is such that several maxima and minima occur in the curves in the spectral region of interest. To obtain a reasonable estimate of the absorption coefficient the measurements should be extended into the region of the absorption band of the material. The substrate should not contribute significantly to the absorption in this region. The effect of random measurement errors will be reduced by combining, in one merit function, the measurements on two or more thicknesses of the material.

In Fig. 2 are shown the normal incidence spectral transmittance and reflectance curves for three different ZnS films on quartz substrates; 15 points from each curve were entered into the merit function. With values 4.81, 0.509, 0.333, and 0.00389 of the constants A, B_1, C_1, and D_1 in the Lorentz dispersion equations [Eqs. (5)] the value of the merit function was 4.1. This implies that the average departure of the calculated data from the experimental measurements was ~2.5%.

To use an analogous approach for determination of the optical constants of low refractive-index dielectric materials, one would have to employ high refractive-index substrates of very low absorption. Instead it is often more convenient to combine the unknown material in a multilayer with known high refractive-index films.

In Fig. 3 we illustrate such an approach. The curves correspond to two 3-layer ZnS/MgF$_2$/ZnS systems with thicknesses chosen so that in the blue part of the spectrum one curve has a maximum and the other a minimum of transmission. This helps to distinguish absorption from interference effects. As in the previous experiment, a mask was used to produce in one deposition run two systems centered on different wavelengths. The merit function was composed of 30 and 15 points from each of the transmittance and reflectance curves, respectively. The optical constants of ZnS were calculated from the parameters determined above. By refinement the merit function was reduced to 3.7.

The refractive indices of medium refractive-index dielectric films are close to those of most substrate materials, and so optical constant determinations from photometric measurements of single films do not yield very accurate results. Again we incorporated the unknown material into a multilayer. But this time we made use of oblique incidence measurements.

The curves in Fig. 4 represent the spectral transmittance at 0 and 45° incidence of a 7-layer system in which MgO films have been combined with MgF$_2$ layers. The merit function was composed of 15 points from each of these curves. The optical constants of MgF$_2$ were calculated from the parameters determined above. Refinement reduced the merit function to 3.0.

We chose this example to illustrate the value of oblique angle measurements. The normal incidence spectral transmittance and reflectance curves of a 7-layer system composed of ZrO$_2$ and MgO layers (Fig. 5) are almost exactly the same as those of the MgO/MgF$_2$ system described before. However, the shift of the features toward shorter wavelengths with angle of incidence is appreciably smaller. Clearly the incorporation of such measurements in the merit function reduces the chances of invalid solutions. After refinement the value of the merit function was 3.8.

In the above examples the optical constants of one material only were determined, and those of the other material were set to the values obtained in a previous experiment. To investigate whether this assumption is justified, we constructed a merit function composed of 90 points chosen from curves 3, 6, 8, 9, 11–16 of Figs. 2–5. The thicknesses of the layers and the dispersion

equation constants obtained in the above determinations served as the starting values for the new calculations. The initial value of the merit function was 3.0. In the refinement process the thicknesses of all the films of all four layer systems and the dispersion equation constants of all four materials were varied simultaneously, and the merit function was reduced to 2.7. The rms changes in the individual thicknesses, refractive indices, and absorption coefficients were only 0.2, 0.2, and 5%, respectively. This indicates that the optical constants of ZnS, MgF_2, MgO, and ZrO_2 found in the separate determinations fit closely the results of the other deposition runs.

B. Metal Films

The optical constants of metal films depend not only on the purity of the starting material but also on the various parameters of the deposition process. Once again it is best to prepare the different films for the determination of the optical constants of a metal in one deposition run with the aid of a suitable mask.

We illustrate the method by determining the optical constants of three Inconel films in the visible part of the spectrum from spectral reflectance measurements at 8° and transmittance measurements at 0 and 45° incidence of light. The thicknesses of the films, as measured with the stylus instrument, were 0.0060, 0.0100, and 0.0200 μm, respectively.

In a first set of calculations a merit function was composed of eight points from each of the four curves for each Inconel film. First, the constants alone of a Drude-Lorentz dispersion equation and then the constants and thicknesses of the three films were refined. The resulting merit functions were 10.3 and 2.7, respectively, and the refined thicknesses were 0.0030, 0.0099, and 0.0220 μm. The high value of the first merit function and the drastically changed thickness of the thinnest layer are a clear indication that the optical constants of the thinnest Inconel film differ significantly from those of the two thicker films. This was corroborated by the fact that a better fit (merit function = 2.2) with essentially unchanged thicknesses could be obtained for the two thicker films alone.

The average values of the optical and dispersion equation constants thus determined are not valid and are, therefore, marked with asterisks in Tables I and II. However, they served as starting points for a second analogous set of calculations on each of the Inconel films (Fig. 6). The final thicknesses (0.0051,0.0099,0.0191 μm) and merit functions (2.1,2.2,2.0) appear reasonable. The resulting dispersion equation constants and optical constants are given in Tables I and II. It will be noted that some of the dispersion equation constants assumed negative values that have no physical meaning. This is of no consequence since, as stated above, the only purpose of the equations is to describe the variation of n and k with wavelength. Furthermore, these latter do not agree well with values quoted in the literature.[34] This may be because of different starting materials and/or deposition conditions. However, the values are

valid for the films produced in our laboratory, for we have designed and successfully constructed a number multilayer metal/dielectric coatings based on them.

We would like to emphasize the point that it is not safe to use spectrophotometric measurements alone to determine simultaneously the optical constants and the thicknesses of thin metal films. An equally good fit to the experimental data (merit function = 2.8) can be obtained if, in the first set of calculations described above, the initial thicknesses of all the layers are doubled! (The resulting thicknesses are 0.0056, 0.0164, and 0.0325 μm, and the average constants are marked with double asterisks in Tables I and II.) The reason for this is that in thin partially transparent metal films the spectral transmittance and reflectance curves do not exhibit marked intensity variations due to interference effects. Thus there is not enough information available for an unambiguous determination of the thicknesses.

C. Semiconducting Films

Figure 7 represents the measured spectral transmittance and reflectance curves of a thin amorphous film of silicon on a glass substrate. The film had a resistivity of 52 Ω-cm.[35] Prior to the determination of the optical constants of this film it was necessary to determine those of the glass substrate. The merit function for the determination of the optical constants of the silicon film consisted of 23 points from each curve of Fig. 7. When the optical constants were represented by the Lorentz equation [Eq. (5)], the merit function could be reduced to 2.50. It is interesting to note that the optical constants of this material can be represented somewhat better by the combined Lorentz and Drude dispersion equation—a merit function of 1.80 was obtained in that case.

We also applied the inverse synthesis method to the determination of the optical constants of indium tin oxide (ITO) films. Two such films of different thickness were deposited onto quartz substrates in one deposition run. Normal incidence transmittance measurements were made for the entire spectral region from 0.35 to 12.0 μm. But because of the limitations of our spectrophotometers and polarizers, reflectance and 45° incidence measurements could only be made in the 0.40–0.80-, 1.0–1.9-, and 2.5–12.0-μm regions. The optical constants were evaluated separately for each of these regions, but in each case the normal incidence transmittance data extended somewhat into the adjacent region (Fig. 8).

The fit between the measured and calculated reflectances and transmittances was good in the 0.35–1.0-μm spectral region. This determination yielded the thicknesses that were used in the calculations on the other regions. Another independent determination based on transmittance and reflectance measurements obtained with extra quartz plates attached to the ITO films with a refractive-index matched contact liquid resulted in essentially the same optical constants and thicknesses. The fit of the 45° incidence data in the 1.1–1.8-μm region was poor. We suspect the mea-

surements were in error because of the poor quality of the polarizers. The fit between some of the measured and calculated data in the 2.5–12.0-μm region was also not very good. The reason for this is probably our inadequate knowledge of the optical constants of quartz which absorbs strongly in this region. The accuracy of the determination could no doubt be improved by use of transparent substrates and more careful measurements. However, our aim was to demonstrate that our method can yield reasonable results even when the measurements are flawed.

VII. Conclusions

We have demonstrated in this paper that the method of inverse synthesis for determination of optical constants is very versatile and can be applied to a variety of optical coating materials. It makes use of commercial analytical equipment of moderate accuracy. The measurements can be made quickly. We estimate that the refractive indices of dielectric coatings can be determined to better than 1% but that the errors in the small absorption coefficients are much larger. This is quite adequate for determination of n and k of materials for use in the construction of a wide range of optical coatings. For laser damage studies the more accurate (and pertinent) calorimetric[36] or photoacoustic[37] methods should be used for determination of the absorption coefficient.

At present in our laboratory the bottleneck in the determination of n and k is the preparation of the data sets for the computer. But we hope to automate this process in the future. It is true that the method requires extensive calculations. However, with present day accessibility to computers and the low cost of computation, this is hardly a consideration.

It is conceivable that with this method cases may be encountered for which a good fit to the experimental measurements on a single film cannot be obtained. One reason for this could be that the optical constants of a particular material cannot be adequately represented by any one set of dispersion equations given in Sec. IV. If no better results are obtained when fitting over a reduced spectral range, chances are that the film is very inhomogeneous. Such films can be approximated by a two- or three-component coating model. If enough experimental measurements are obtained a solution can be sought on this basis.

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