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Thin Solid Films 354 (1999) 176–186

thin solid films

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Simultaneous measurement of spectral optical properties and thickness of an absorbing thin film on a substrate

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Received 15 March 1999; received in revised form 20 July 1999; accepted 20 July 1999

Abstract

This paper describes a technique and also illustrates an application of the technique for simultaneously measuring both the spectral complex refractive index (n_1, k_1) and the thickness d_1 of an absorbing thin solid layer on a thick substrate. The contours of constant reflectance R and transmittance T in the (n_1, k_1), (n_1, d_1) and (k_1, d_1) planes are examined for a thin layer on a substrate, which is exposed to oblique unpolarized incidence, under various conditions in order to facilitate an optimal choice of the combination of measured quantities for the inverse estimation of parameters. Theoretical analysis illustrates that optimal choices would include measurement of R at a large angle of incidence, combined with measurements of normal T and near normal R so as to reduce erroneous solutions or nonconvergence. And any additional measurement R at any angle of incidence may be used to prevent the multiple solutions. For the inverse estimation of parameters, we also present a technique in association of the least squares method to extract the thickness and optical constants characterizing the thin absorbing film from measurements of R and T. The method is then applied for experimental measurement of the optical properties and thickness of a polyvinylalcohol (PVA) film placed upon a substrate of ZnSe. These results provide useful information for analyses on the applications of PVA in textile sizing, adhesives, polymerization stabilizers, and paper coating. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Absorbing media, Refractive index; Spectral dependence; Polyvinylalcohol

1. Introduction

The determination of the optical properties of thin films is a topic of fundamental and technological importance. The currently soaring interest in solar absorption, temperature control, radiative cooling, etc. has further created a demand for routine techniques to determine the optical constants of absorbing coating materials in the visible and infrared wavelength regions. Determination of the complex refractive indices for polymer films is also of interest in the study of photothermal solar energy conversion, the design of hollow waveguides and electric conductors, as well as for the use of evaporated films in space applications. To analyze heat and mass transfer in the drying processes of polymer solutions by infrared radiant heating, one is also most interested in the absorption of a polymer and the reflectance at an interface [1]; and the simplest way to examine absorption is to know the complex refractive index of the polymer. The extraction of the optical constants and thickness of films from various types of optical measurements is a field of widespread interest, and the derivation of precise values for these indices has been the subject of numerous studies. Measurements of reflectance R and transmittance T of a film can yield values of the optical constants n and k. However, accurate evaluation of the refractive index (n, k) from R and T values is a complex task, due to the highly nonlinear relationships among the variables involved and the singularity of the solutions. Methods for determining the optical constants and thickness of partially absorbing specimens have usually involved measurements of transmittance and reflectance at normal or oblique incidence, measurement of transmittances of specimens at various values of thickness, measurement of reflectances at several incident-angles or different combinations of them.

Many methods for the optical analysis of a thin film deposited onto a thick substrate with finite thickness have

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0040-6090/99/$ - see front matter
PII: S0040-6090(99)00530-1

been published. Vriens and Rippens [2] used $(1 \pm R)/T$ or $(1 \pm R')/T$ functions to deduce n and k of a thin solid film on a slightly absorbing substrate with use of an iterative method. In their analysis, transmittance T, the air-incident reflectance R and substrate-incident reflectance R' are utilized. Elizalde and Rueda [3] determined the optical constants for metallic and semi-conducting films from measurements of normal T, oblique R and T with perpendicular and parallel polarization components. T, R and R' were measured by Chang and Gibson [4] to locate the correct values of n and k and the sensitivity of n and k determinations to measurement errors was investigated. Minkov [5] used the reflectance spectrum for different angles of incidence of nonpolarized or s- or p-polarized light to compute the optical constants and thickness of thin films. The extreme value of the R spectrum was required to find the solutions. Swanepoel [6] evaluated the optical constants and the thickness of a coating layer from the transmission spectrum alone. An interference fringe pattern method was used to find the Cauchy's forms of complex refractive index. Similar research was also found in the works of Kubinyi et al. [7] and Wang and Miyagi [8]. Most of the previous works included systems which involved an absorbing thin film deposited on a transparent substrate [3,4,6–8] or normally incident light [2,6–8]. While considering the measurements of both the optical constants and film thickness, they all proposed methods which determine the optical properties and thickness separately [3,6–8].

There are often practical problems with the inverse method. Specifically, in some cases the solutions are not unique for given measured quantities, or the accuracy of the solutions is questionable even though the experimental data are very precise. Due to the numerical complication of inversion, some works had been done on the choices of suitable combinations of measurements for the inverse estimation of the optical properties. Nilsson [9] took into account the functional dependencies of n and k on R, R' (the reflectance of the substrate side) and T at normal incidence for a film on a transparent substrate. It is found that the combination of R and T was the best one in order to calculate the complex refractive index. Cisneros et al. [10] also examined a similar relationship for the complex refractive index of thin films at normal incidence. The thicknesses at the extreme in the reflectance curves were used to exclude the incorrect solutions. Nestell and Christy [11] discussed the behavior of R and T under different conditions of polarization, incident angle, and film thickness, in order to facilitate a choice of the best combination of measurements on thin films. They showed that a judicious choice of incident angle and polarization can cope with some troublesome regions of $n - k$ space where normal incidence measurements are inaccurate. The (R_m, T) normal incidence method presented in Hjortsberg's work [12] was based on a new substrate configuration which removes the contour tangency problem of the (R, T) method. R_m is the near normal reflectance of the film on the metallized part of the substrate. In his work, a transparent substrate must be partially covered with a highly reflecting metal, and the thin film must then be deposited over the entire substrate area. Hunderi [13] found that systematic errors for obtaining optical constants of a material could be greatly reduced based upon measuring the relative derivative of the reflectance with angle of incidence $(1/R)(dR/d\theta)$. Denton et al. [14] had analyzed the equations expressing $(1 \pm R)/T$ in terms of the film and substrate parameters for both single- and double-layer films. They showed that multiple solutions of these equations may make measurements at a single wavelength useless for inverting data but contain important information concerning film thickness, provided measurements are made over a wide range of wavelengths. In these studies [9–14], either a mathematical reformulation of the system or a transformation of experimental quantities is introduced to remove the multivalued or incorrect solutions. These effects, however, either make the problem more complicated or may not completely remove the ambiguity. The above studies intend to obtain a best choice of the combination of experimental quantities on thin films from the contour maps of two various measurements in the (n, k) plane. To simultaneously measure both the complex refractive index and the thickness d, it is significant to comprehend the effects of refractive index and film thickness on R and T. However, a detailed investigation on the influences of (n, d) and (k, d) on reflectances and transmittances of an absorbing thin film on an absorbing thick substrate at oblique incidence is not found in previous studies.

In this paper, we are motivated to accurately determine the optical constants as well as the film thickness of an absorbing thin film on an absorbing substrate. An analysis on the contours of constant reflectance R and transmittance T in the (n_1, k_1), (n_1, d_1) and (k_1, d_1) planes is presented for a thin layer on a substrate, which is exposed to oblique unpolarized incidence, and a technique is developed for the simultaneous estimation of both the complex refractive index and the film thickness. Using the laws of electromagnetism, we derive analytical expressions for the transmittance and reflectance of a coated layer on a substrate of finite thickness. Multiple reflections at the three interfaces, which are coherent in the thin film and incoherent in the thick substrate, are considered. We examine the behavior of R and T under various conditions of incident angle and film thickness, in order to promote a choice of the optimal combination of measurements on films. We also examine the effects of n_1, k_1 and d_1 on R and T curves at various angles of incidence. Besides, the method of least squares is utilized and an inverse analysis is presented, that inverts the functions R and T to give the optical constants and thickness of the film. Since little data concerning the optical properties of PVA are available in the infrared region, the method is applied to a PVA film placed on a ZnSe substrate in the 2.5-21.5 μm wavelength range. Experimental results presented herein are compared with the data taken from previous investigations.

2. Mathematical model

We consider that a parallel monochromatic beam of unit amplitude and of wavelength λ at an angle of incidence φ_0, which is measured with respect to the normal, impinges upon an optically homogeneous, isotropic absorbing film bounded by plane parallel surfaces. This thin film is of thickness d_1 and supported by an optically homogeneous, isotropic absorbing substrate of thickness d_2. It is assumed that the thickness of the absorbing film is comparable with the wavelength while the substrate is of a significantly greater thickness than the coherence length of the incident wave. These two media are characterized optically by their refractive indices n_i and absorption coefficients α_i, which are contracted in the complex refractive indices $\hat{n}_i (= n_i + ik_i)$ and $k_i = \alpha_i \lambda / 4\pi$. Both the boundaries of the two media are ideally flat and smooth. The refractive indices of the two ambient media are n_0 and n_3, respectively. This system of thin film/substrate assembly is shown in Fig. 1. Multiple reflections at the three interfaces (air-film, film-substrate and substrate-air), which are coherent in the film and incoherent in the substrate, must therefore be considered. According to the notation of Heavens [15], r_{01} and t_{01} are the Fresnel coefficients, which respectively represent the ratio of the reflected and incident (r) and that of the transmitted and incident (t) electric-field amplitudes at the interface as the incident beam travels from medium n_0 to medium $\hat{n}_1$. r_{01} and t_{01} are the Fresnel coefficients as the beam travels from medium $\hat{n}_1$ to medium n_0. In accordance with the laws of electromagnetism, the Fresnel reflection and transmission coefficients (composed of perpendicular and parallel components) are expressed as

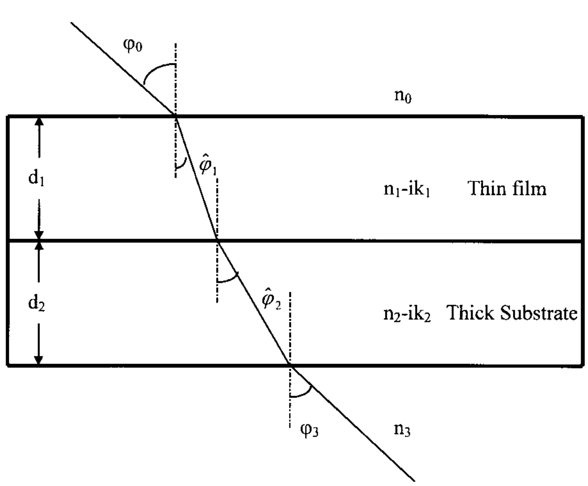

Fig. 1. Schematic representation and notation of current study.

$$r_{10,s} = \frac{n_0 \cos\varphi_0 - \hat{n}_1 \cos\hat{\varphi}_1}{n_0 \cos\varphi_0 + \hat{n}_1 \cos\hat{\varphi}_1} \tag{1}$$

$$r_{10,p} = \frac{n_0 \cos\hat{\varphi}_1 - \hat{n}_1 \cos\varphi_0}{n_0 \cos\hat{\varphi}_1 + \hat{n}_1 \cos\varphi_0}$$

$$t_{10,s} = \frac{2 n_0 \cos\varphi_0}{n_0 \cos\varphi_0 + \hat{n}_1 \cos\hat{\varphi}_1} \tag{2}$$

$$t_{10,p} = \frac{2 n_0 \cos\varphi_0}{n_0 \cos\hat{\varphi}_1 + \hat{n}_1 \cos\varphi_0}$$

where $\hat{\varphi}_1$ denotes the angle of refraction for a wave propagating from medium n_0 to a medium with refractive index $\hat{n}_1$ and is defined by Snell's law $\hat{n}_1 \sin\hat{\varphi}_1 = n_0 \sin\varphi_0$. Subscripts s and p represent the polarized components respectively perpendicular and parallel to the plane of incidence. These Fresnel coefficients are explicitly expressed in Appendix A.

We first consider systems of a thin film only before examining the reflection and transmission characteristics of a thin film on a substrate. Since the thickness of the film is comparable with the wavelength of incidence, interference effects become significant. Interference effects within the film are normally represented by infinite sums over the amplitude of contributing waves. Then the reflectance of the film on the air-side boundary R_{02} and substrate-side boundary R_{20}, and its transmittance on its substrate-side boundary T_{02} and air-side boundary T_{20}, can be obtained by summing the electric fields of the multiply reflected beams in the coherent limit. For a beam of unit intensity with s polarization incident on the film/substrate assembly in the direction air-film-substrate, the intensity reflected back after coherent multiple reflections at the air-film and film-substrate interfaces is given by [15]

$$R_{02,s} = \left| \frac{r_{01,s} + r_{12,s} exp(-2i\delta_1)}{1 + r_{01,s} r_{12,s} exp(-2i\delta_1)} \right| \tag{3}$$

The reflectance of the film/substrate assembly to a beam incident in the direction from substrate to film is similarly given by

$$R_{20,s} = \left| \frac{r_{21,s} + r_{10,s} \exp(-2i\delta_1)}{1 + r_{21,s} r_{10,s} \exp(-2i\delta_1)} \right|^2 \tag{4}$$

The corresponding expressions for the transmittances are given by

$$T_{02,s} = \frac{Re(\hat{n}_2 \cos\hat{\varphi}_2)}{n_0 \cos\varphi_0} \left| \frac{t_{01,s} t_{12,s} \exp(-i\delta_1)}{1 + r_{01,s} r_{12,s} \exp(-2i\delta_1)} \right|^2 \tag{5}$$

$$T_{20,s} = \frac{n_0 \cos\varphi_0}{Re(\hat{n}_2 \cos\hat{\varphi}_2)} \left| \frac{t_{21,s} t_{10,s} \exp(-i\delta_1)}{1 + r_{21,s} r_{10,s} \exp(-2i\delta_1)} \right|^2$$

where δ_1 denotes the change in phase of the beam on traversing the film, and is expressed as

$$\delta_1 = \frac{2\pi}{\lambda}\hat{n}_1 d_1 \cos\hat{\varphi}_1 \tag{6}$$

$\exp(-i\delta_1)$ in the expressions accounts for both the phase and the attenuation in the film due to absorption. $Re(\hat{n}_2\cos\hat{\varphi}_2)$ means the real part of function $\hat{n}_2\cos\hat{\varphi}_2$.

In contrast to the film, the thickness of the substrate is larger by orders of magnitude than the coherent length of the incident wave, i.e. which is at the incoherent limit, interference effects on reflection are not included in the substrate. And

$$R_{23,s} = |r_{23,s}|^2 \tag{7}$$

$$T_{23,s} = 1 - R_{23,s}$$

where R_{ij} and T_{ij} with $j = i \pm 1$, respectively, are the reflection and transmission at interface between the optical media designated by i and j when they are assumed to be semi-infinite.

If the film/substrate assembly is considered, the incident ray is partly reflected at angle φ_0 and partly transmitted at an angle $\hat{\varphi}_1$. The transmitted portion upon arrival at the film-substrate interface is again partly reflected and partly transmitted. The similar phenomena can be seen while the latter transmitted portion arrived at the substrate-air interface. After multiple coherent reflections at the air-film and film-substrate interfaces the beam of intensity T_{20} suffers multiple incoherent reflections at the substrate-air interface and the substrate-film plus film-air interface. The perpendicular components of reflectance and transmittance of the system under investigation can be obtained by summing the intensities of the multiply reflected beams. They are expressed as [3]

$$R_s = R_{02,s} + \frac{T_{02,s}T_{20,s}R_{23,s}A_0^2}{1 - R_{20,s}R_{23,s}A_0^2} \tag{8}$$

and

$$T_s = \frac{T_{02,s}T_{23,s}A_0}{1 - R_{20,s}R_{23,s}A_0^2} \tag{9}$$

where $A_0 = \exp\left[-4\pi Im(\hat{n}_2\cos\hat{\varphi}_2)d_2/\lambda\right]$ is the absorption in the substrate. In addition, the parallel components of reflectance and transmittance are expressed by the similar form as Eqs. (8) and (9). If the substrate alone in the absence of a film is considered, the perpendicular components of reflectance and transmittance of the bare system under investigation can be expressed by

$$R_{b,s} = R_{23,s} + \frac{T_{23,s}^2 R_{23,s}A_0^2}{1 - R_{23,s}^2 A_0^2} \tag{10}$$

and

$$T_{b,s} = \frac{T_{23,s}^2 A_0}{1 - R_{23,s}^2 A_0^2} \tag{11}$$

Eqs. (10) and (11) are consistent with the results of Eqs. (8) and (9) at n_1, k_1, and d_1. Thus, for unpolarized incidence, the reflectance and transmittance are the averages of both perpendicular and parallel components, i.e.,

$$R = \frac{R_s + R_p}{2} \text{ and } T = \frac{T_s + T_p}{2} \tag{12}$$

Since R_s, R_p, T_s, T_p, R and T are only function of the complex refractive index with known wavelength of incident wave and thicknesses of films, the analytical expressions for the dependencies of R and T on the real and imaginary parts of the refractive index (n_i and k_i, respectively), the wavelength of incidence λ, the film thickness d_i, and the angle of incidence φ_0 are thus deduced.

3. Computational methodology for inversion estimation of parameters

In the present study, the least squares method is used to simultaneously determine the complex refractive index (n_i, k_i) and the thickness d_i with known reflectances and transmittances at various angles of incidence, where i can be (1) if a thin film on a thick substrate with known optical constant and thickness is considered or (2) if the properties of the substrate are to be measured. We let a function E be defined as

$$E = \sum_{i=1}^{n}\left[\left(T_{i,c} - T_{i,e}\right)^2 + \left(R_{i,c} - R_{i,e}\right)^2\right]$$
$$= \left[Y - \eta(\beta)\right]^T\left[Y - \eta(\beta)\right] \tag{13}$$

where $R_{i,e}$ and $T_{i,e}$ respectively denote experimental measurements of reflectances and transmittances for any angle of incidence. $R_{i,c}$ and $T_{i,c}$ are the theoretical values of reflectances and transmittances for any angle of incidence. Let

$$Y(i) = \begin{bmatrix} R_{1,e} \\ T_{1,e} \\ \vdots \end{bmatrix} \text{ and } \eta(\beta) = \begin{bmatrix} R_{1,c}(n,k,d) \\ T_{1,c}(n,k,d) \\ \vdots \end{bmatrix} \tag{14}$$

where $\beta = n, k, d$. Closely examining the function E in the plane defined by the complex refractive index and thickness of film reveals that, for every value of d, there exist the values of n and k for which E is minimum. The partial derivative of E with respect to β ($\beta = n, k$ or d) is expressed as

$$\nabla_\beta E = 2[-\nabla_\beta \eta(\beta)]^T[Y - \eta(\beta)] \tag{15}$$

and we let

$$X(\beta) = [\nabla_\beta \eta(\beta)]^T \quad (16)$$

where X is termed the sensitivity matrix, and the elements of this matrix are called the sensitivity coefficients [16]. While $\nabla E = 0$, the minimum value of E exists. Therefore, we are looking for a set of solutions, $\hat{\beta}$, so that

$$X^T(\hat{\beta})[Y - \eta(\hat{\beta})] = 0 \quad (17)$$

Taking the Taylor expansion of $\eta(\hat{\beta})$ at b, we have

$$\eta(\hat{\beta}) = \eta(b) - \nabla\eta(b)(\hat{\beta} - b) \quad (18)$$

By substituting Eq. (18) into Eq. (17), Eq. (17) is then rewritten as

$$X^T(b)[Y - \eta(b) - X(b)(\hat{\beta} - b)] \approx 0 \quad (19)$$

Equation (19) is applied in the numerical computation of the inverse estimation of parameters. We start the iteration with initial guesses of b. After iterating k times, the $(k + 1)$ th iteration is then started with the new parameters

$$b^{(k+1)} = b^{(k)} + P^{(k)}[X^{T(k)}(Y - \eta^{(k)})] \quad (20)$$

and

$$[P^{(k)}]^{-1} = X^{T(k)}X^{(k)} \quad (21)$$

The computation will continue until a satisfactory match is achieved. Physically, $b$in the expression represents the guessed value for $\hat{\beta}$, that is, $\beta = n, k, d$ as defined earlier. In order to save the computational time, the convergent values of $n_i(\lambda_n)$, $k_i(\lambda_n)$, and $d_i(\lambda_n)$ could be used as the initial guesses of $n_i(\lambda_{n+1})$, $k_i(\lambda_{n+1})$, and $d_i(\lambda_{n+1})$.

4. Experimental arrangement

To illustrate the application of the present analysis, we employ a polyvinylalcohol (PVA) film on a ZnSe substrate of 1mm thickness and 13 mm (half a inch) diameter and results of inverse analysis are compared to existing results. The PVA film is prepared by solution poured on one side of the ZnSe substrate. Concentration of PVA solution of 2% by weight polymer is made by using still water as solvent. We subsequently place the sample in an infrared dryer and it is baked at the temperature of 60°C for 6 h to remove solvent. The heating temperature of the dryer and the heating time during drying process are controlled due to the reason that thermal field in solution may significantly affect the quality of the PVA film. Since 99.5 ± 0.3% of the solvent weight loss is detected after the heating process, we thus ignore the effect of absorption of water on the measurements of infrared spectra. The spectral dependencies of the transmittance and reflectance in the range from 2.5 μm to 25 μm are measured by a Fourier Transform Infrared Spectrometer of model BIO-RAD FTS-40 at a resolution of 4 cm^{-1}. This apparatus measures the transmittance at normal incidence and the reflectance at an arbitrary oblique angle with a variable angle specular reflectance (VASR) accessory. This accessory allows continuous change of the angle of incidence for a very broad range of angles, which is theoretically up to 85°. Unfortunately, it is not feasible to construct accessories to work at such high angles since the infrared beam will spread across the sample and large samples are required to collect the incident energy of infrared beam. Once the initial alignment is set, the VASR accessory remains in alignment for all other set angles of incidence. A gold mirror is used as the reference specimen for the reflectance measurement. The single-beam IR transmittance and reflectance spectra are collected (64 scans) with the use of unpolarized infrared incidence and stored on the computer disk. Normal incidence transmittance T and three reflectance measurements R at 15, 60 and 75° angles of incidence within a wavelength range of 2.5–22.5 μm are made for a PVA film on the substrate of ZnSe and also for a bare substrate. Sampling points at every 0.25-μm interval are used in our calculations for inverse estimations of parameters. The repetitive error of measured results is shown to be below 5%.

5. Results and discussion

Our main focus is not only on the mathematical techniques of estimating the optical constants and film thickness from given experimental data, but also on the optimal choice of experimental input quantities. According to the above derived formulae, R and T are single-valued functions of n_1, k_1 and d_1, but it turns out that n_1, k_1 and d_1 are multiple-valued functions of R and T. Therefore, the expressions for R and T must be further understood before applied for parameter estimation. Although any two independent measurements of transmittance and reflectance with specified polarization, incidence angle and wavelength are theoretically sufficient to determine the two parameters n_1 and k_1, the degree of accuracy in the determined optical constants is critically dependent on the choice of experimental entities. We thus discuss the behavior of R and T under different conditions of incident angle and film thickness, in order to promote a choice of the optimal combination of measurements on films.

In the following results of numerical analysis, the indices of ambient dielectric media, n_0 and n_3, are both equal to 1.0, and the complex refractive index and thickness of the substrate are given as $n_2 = 1.5$, $k_2 = 10^{-5}$, and $d_2 = 1000\ \mu m$. The wavelength of the incident ray, λ, equals 500 nm. If not specified, solid lines refer to the contours of constant R and dashed lines to the contours of constant T in figures. Results are given for specified values of incident angle, ratio of the thickness of film to wavelength of incident ray, and the optical properties of substrate, as well as its geometric thickness. Fig. 2 shows such contour plots for the normal reflectances and transmittances, R and T, when the ratio of the thickness of film

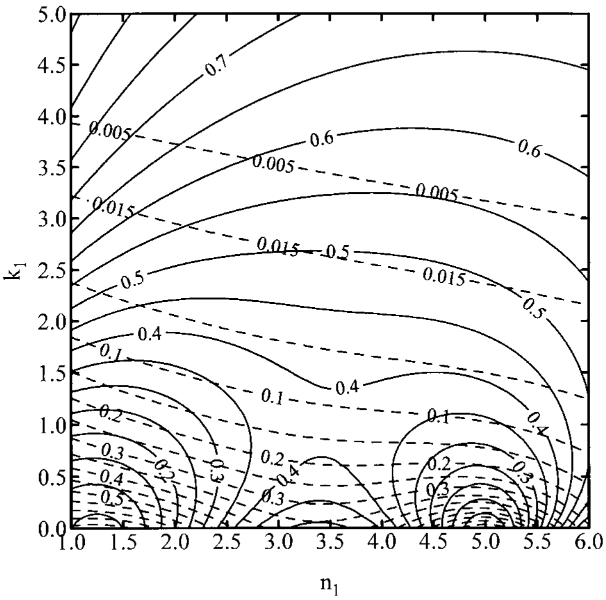

Fig. 2. Contours of constant R and T for normal incidence and $d = 0.1$.

to wavelength of incident ray, $d(= d_1/\lambda)$, is equal to 0.1. They are plotted against the real part of complex refractive index of film, n_1, and the imaginary part of complex refractive index of film, k_1. It is found that for larger k_1 R increases as k_1 increases but decreases then increases as n_1 increases. While for small k_1, oscillations occur in the variations of R with n_1. This implies that there exist several values of n_1 corresponding to a small R when k_1 is constant, but we observe that there is only one n_1 corresponding to a large R. Thus multiple-solution regions could be found where k_1 is small. The multiple-solution regions also represent the regions where the constant R and T contours intersect at two or more than two points and may not be able to acquire the exact results of n_1 and k_1. Similarly, the results can be illustrated as we interchange k_1 with n_1. Therefore, if a material has high reflectances, there only exists one set of n_1 and k_1. It is also noticed that near the region of small k_1 there exist branch points where the R and T curves are tangent to each other. This indicates that a single solution does not exist for all pairs of R and T. Around these branch points that angle between the R and T curves is very small and small experimental errors may lead to results of large errors (especially in n_1) or even to nonconvergence. Also parameter estimation with only R and T may result in multiple solutions. According to Fig. 2, T decreases as n_1 or k_1 increases with k_1 or n_1 maintaining constant, and T will finally approach to zero. The transmittance value is evidently determined almost solely by the imaginary part of the refractive index k_1 whereas the dependence of the real part of the refractive index n_1 is very weak. While k_1 is large and the gradient of curves T is very small, it is difficult to find out exact values of n_1 and k_1, since a small experimental error can significantly influence the accuracy of results. Thus, the absolute error in the inferred n_1 and k_1 is large due to the small gradients of the distributions of the measured quantities and uncertainties in the measured R and T values. Furthermore, T is a monotonically decreasing function when k_1 is not very small. With known transmittances, n_1 and k_1 can be determined once one of them is readily found.

There are two practical problems with the above (R, T) method. First, the solutions are not unique for a given measured (R, T). This multivaluedness, which is an inherent property of any technique using two intensity measurements, produces a real problem in the (R, T) case in regions near the contour tangency points, which are branch points between different solutions. The absolute error in n_1 and k_1 is large where the sets of two contours are tangent to each other. This ambiguity may be removed through the additional experimental quantities [3] or a mathematical reformulation [13] of the problem. Second, the contours of R and T often intersect at very small angles, so that the accuracy of the solutions is problematic even when the measured data are accurate. Consequently, even a minor experimental error in such regions leads to gross errors in the extracted optical constants. To obtain an accurate estimation of n_1 and k_1, better experimental measurements would include those with contours nearly perpendicular to each other. The accuracy of the determined optical constants and film thickness is governed by two factors, namely, by the gradients of the distributions of the measured quantities and by the intersection-angle of the contours. Larger gradients and/or intersection-angles clearly yield higher accuracy.

In Fig. 2, we notice that the angle of intersection between the R and T curves is small in some regions. Thus, some

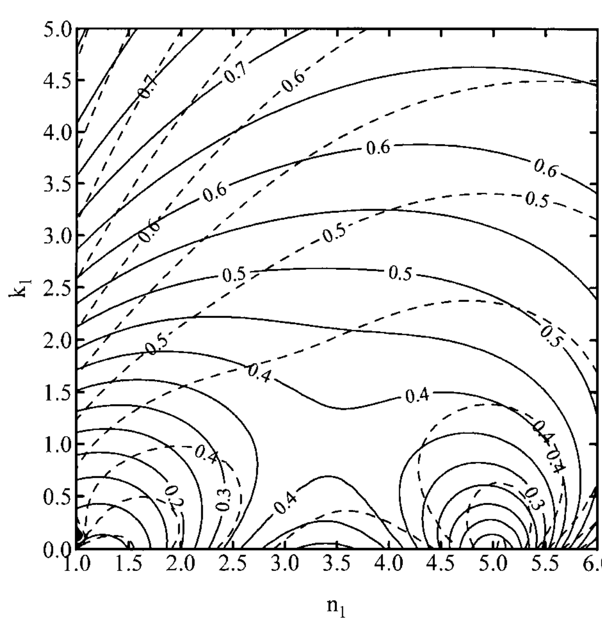

Fig. 3. Contours of constant R for 75° angles of incidence and $d = 0.1$.

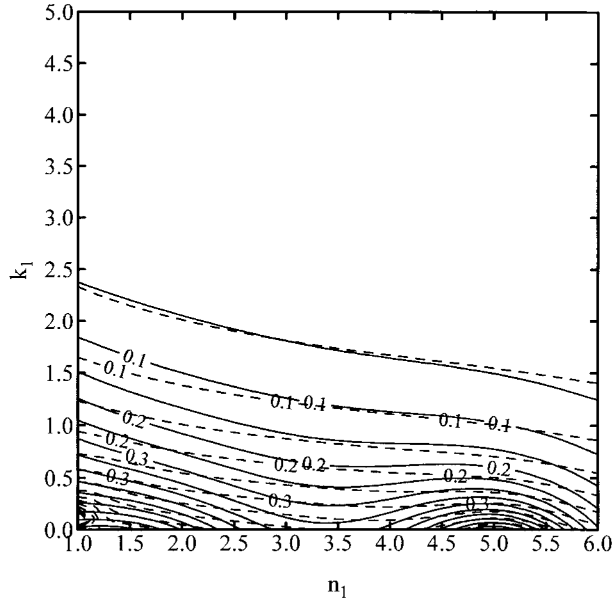

Fig. 4. Contours of constant T for 75° angles of incidence and $d = 0.1$.

experimental errors may cause large errors in n_1 or even numerical nonconvergence during inverse process for parameter estimation from measured R and T. Similar contours of R and T are obtained as optical constants and/or thickness of the substrate varies. At oblique incidence, a plot of R and T contours also shows the same features as shown in Fig. 2. The tangency of R and T contours still occurs and multiple intersections appear. In order to understand the behavior of R at different incident angle, we plot contours of constant R at different angle of incidence in the (n_1, k_1) plane, as shown in Fig. 3. We also plot in Fig. 4 the contours of constant T at different angle of incidence in the (n_1, k_1) plane. d for both figures is equal to 0.1. The solid lines refer to the normal incidence, R_0 or T_0, and the dashed lines to the 75° angle of incidence, R_{75} or T_{75}. It is shown in Fig. 3 that in the region of large k_1 the curves (R_0, R_{75}) intersect at a relatively larger angle. Therefore, one may accurately estimate the optical properties for materials of high k_1 with the measured data of R_0 and R_{75}. While in the region where k_1 is small, one may easily obtain multiple solutions due to the fact that two curves may intersect at a very small angle or even be parallel. In such a case, one cannot acquire the exact results of n_1 and k_1 unless n_1 of the film to be measured is readily known. Similar analysis can also be done on the distributions of transmittance. It is found in Fig. 4 that T_0 and T_{75} are approximately parallel and thus there would exist multiple solutions or result in a solution with large error in the parameters estimation with measurements of transmittance. It is clear from the comparison that the combination of reflectances at different angles of incidence would be preferred rather than the combination of transmittances for determining the optical constants, provided that the thickness of the film is specified.

In regard to simultaneous measurements of both optical constants and thickness of a thin film, we also examine the contours in the (n_1, d) plane. Fig. 5 displays contours of normal R and T for $k_1 = 1.0$. It is shown that there exist oscillations of R varying with d at constant n_1 and R eventually approaches to an asymptotic value as d is large enough. This asymptotic value of R varies with n_1 and is increased as n_1 increases. It is found that R and n_1 have a linear relationship as d is large enough. Similar investigation is also presented for the contour plots of transmittance T in Fig. 5. It is noticed that T increases as d and/or n_1 decreases. It should be pointed out that in the region where d is small, the intersection angles between the contours (T,R) are extremely small and thus one would easily obtain multiple solutions or a solution with large error in the estimation of parameters (n_1, d). The contours of constant R and T in the (k_1, d) plane for normal incidence and $n_1 = 2.0$ are shown in Fig. 6. This figure reveals that variation of R with d at a given value of k_1 is like a damped sinusoid. The oscillation ceases as d is large and R approaches a constant value. The value is larger as k_1 is larger. The trend of the variations in T is similar to that of R and the only difference is that T approaches zero as d is large. It is also illustrated in the figure that the contours (T,R) intersect at more than one point as k_1 is small or intersect at an extremely small angle as d is very small. Consequently, it would lead to multiple solutions or a solution with large error in parameters estimation with use of measurements of normal (T,R).

In the following, we examine in detail the distributions of R-vs-φ_0 and T-vs-φ_0 curves at various values of n_1, k_1 and d. As illustrated in Fig. 7, the magnitude of R is only slightly changed with φ_0 as φ_0 increases but increases

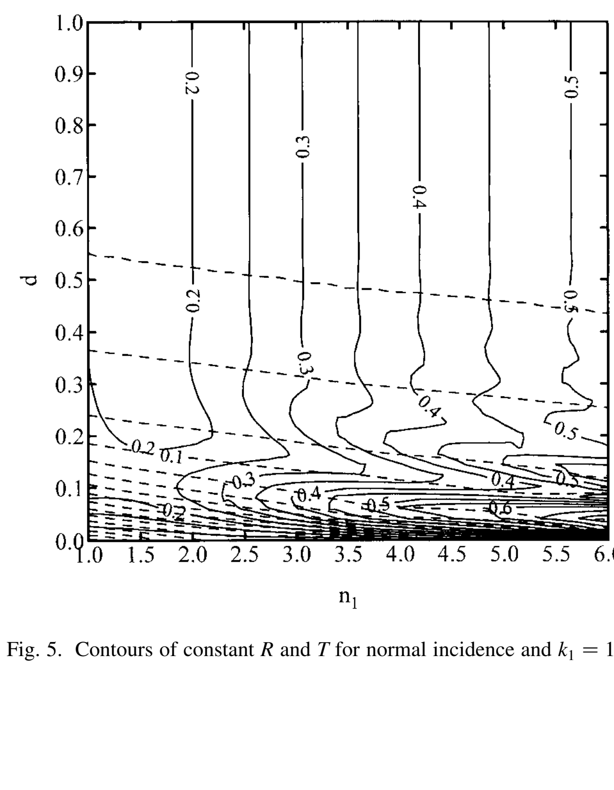

Fig. 5. Contours of constant R and T for normal incidence and $k_1 = 1.0$.

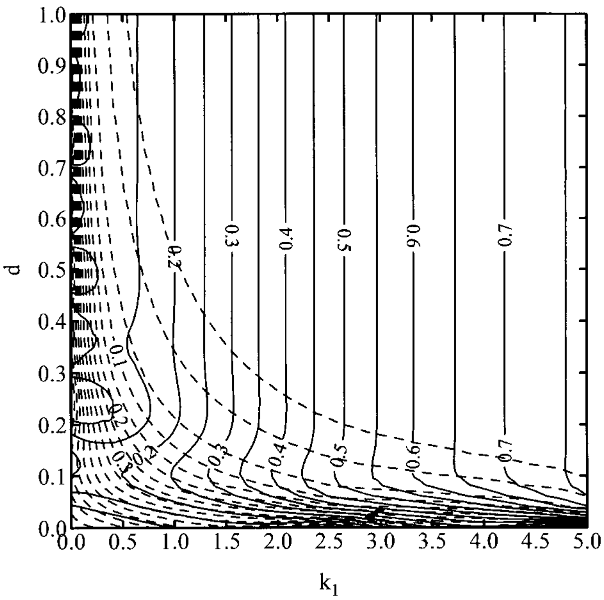

Fig. 6. Contours of constant R and T for normal incidence and $n_1 = 2.0$.

abruptly when φ_0 is larger than 60°. T slightly decreases as φ_0 increases and then rapidly approaches to zero as φ_0 is further increased. The influence of optical constants and film thickness on R and T is not distinct at angle of oblique incidence below 60°. It should be mentioned that the method of inversion for parameter estimation with R and T at large incidence angle would be sensitive to the experimental accuracy of the incident angle. Therefore, a small error in angle in experimental measurements at large angle of incidence could result in a huge discrepancy in measured quantities of R and T. It is also noticed that at larger angles of incidence the reflectance is not sensitive to the absorption index and the effect of the real part of the complex refractive index on transmittance is not significant. Inverse estimation with only measurements of transmittance and reflectance at larger angle of incidence may not be suitable. From the above analysis, it is concluded that an optimal choice of measurements for inverse parameters estimation would include normal R and T associated with a R measured at a larger angle of incidence.

In experimental measurements for simultaneous determination of optical constants and thickness of a thin film, at least three measurements should be required since there exist three unknowns (complex refractive index and sample thickness). From the above analysis, it is suggested that R measured at a large angle of incidence, combined with normal T and near normal R (since R at normal incidence can not be measured in reality) are utilized to reduce numerical erroneous solutions or nonconvergence in numerical inversion. Since the inverse problem is ill-posed, optical constants and film thickness may be multiple-valued functions of R and T. This ambiguity can be removed through any additional measurement of R or T. In the present analysis, the optical experiments consist of a measurement of normal incidence transmittance T of the sample and three reflectance measurements R at 15, 60 and 75° angles of incidence..

As a substrate on which the PVA films are to be coated, we have selected ZnSe, which is slightly absorbing between the infrared wavelengths 0.8 μm and 21.5 μm. The measured spectral dependencies of the reflectance curves at three different angles of incidence and the normal transmittance curve corresponding to a bare ZnSe substrate are analyzed with the method developed herein. From our calculations, the optical constants and thickness with representative error bars of the specimen of ZnSe are presented within a wavelength range of 2.5–21.5 μm, as shown in Fig. 8. The continuous lines represent the average values of optical constants and thickness extracted from three sets of experimental measurements. The transmittance data are extremely small beyond 21.5 μm and thus the results cannot be obtained due to numerical divergence during the inversion process. It is noticed that there exists a satisfactory coincidence of n_2 and k_2 between our results and existing data [17]. The results of n_2 also agree well with those published by Saito et al. [18] and the thickness d_2 is in good agreement with that $d_2 = 1000$ μm (according to the manufacturer specifications). Application of the inversion method proposed here is shown to be satisfactory for accurately evaluating the complex refractive index and thickness of a single layer and the method is then applied to an assembly of a PVA thin film on a ZnSe substrate. In the top part of Fig. 9, the curve manifests the normal transmittance spectrum to a PVA film as published by previous investigators [19], while in the lower portion of

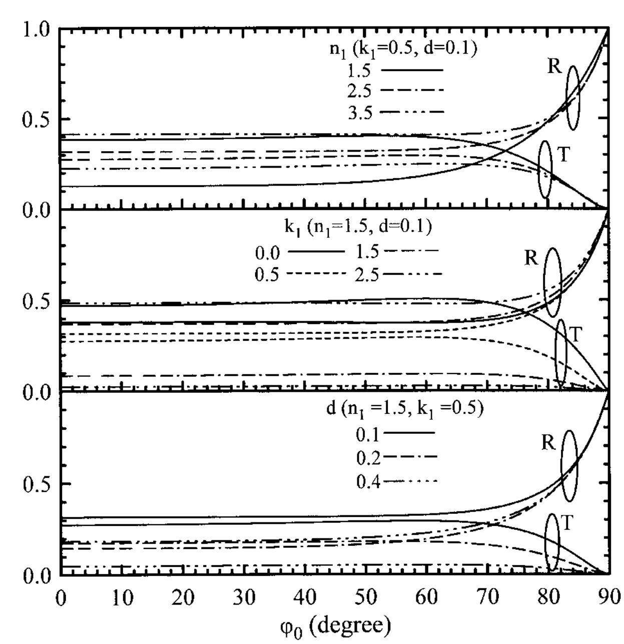

Fig. 7. R and T as functions of incident angle φ_0 in degrees.

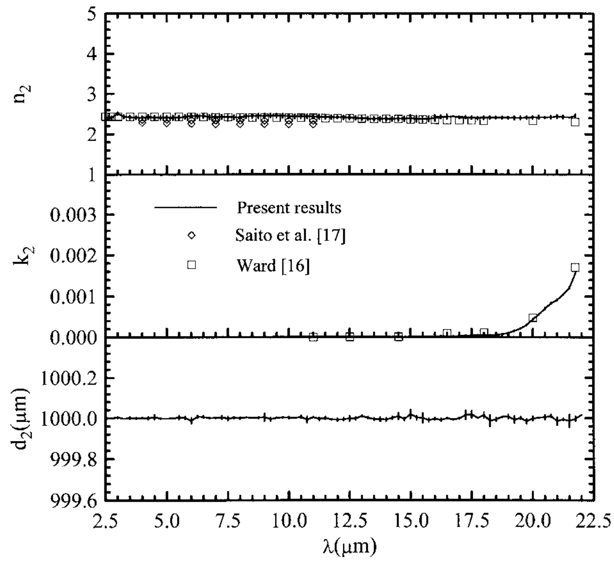

Fig. 8. Optical constants and thickness for a substrate of ZnSe.

the figure four different curves respectively illustrate the normal transmittance spectrum and reflectance spectra at three different angles of incidence for a PVA film on a substrate of ZnSe from our experimental measurements. It is found that the absorption peaks lie in the same bands between two portions of the figure. In inverse analysis for parameters estimation, the optical constants of the substrate are taken from the average data determined in the current study, as shown in Fig. 8. Using the spectral dependencies of the measurements of the PVA-film/ZnSe-substrate system shown in Fig. 9 together with those of the optical constants and thickness of the substrate, the spectral complex refractive index and thickness of the PVA film are determined. Fig. 10 illustrates the results of the optical constants and thickness with representative error bars for the PVA film. The energy is almost absorbed in this system above $\lambda = 22.0$ μm, and the solutions among these bands are difficult to derive because of the numerical difficulty mentioned earlier. In previous investigations [20–22], the values of n_1 are found to be in the range from 1.49 to 1.55. The obtained value of the real part of the optical constants, n_1, in the present study is in reasonable coincident with those reported. There exist some deviations of k_1 between existing data [20] and the present results, especially in the strong absorption bands of 5.8 μm, 6.4 μm and 7.5 μm. In Fig. 9, these three absorption peaks can be found in both the present study and work in [19], but not shown in the results presented by Nishimura et al.[20]. The average thickness of the PVA film is 8.521 μm, and the maximum variation in the thickness measurement is about 8.57%. Since the repetitive error of measured results of (T,R) is under 5%, the variation might be mainly caused by an inhomogeneity of the film, a non-smoothness of the film surface, or a nonuniformity in thickness across the film.

6. Conclusions

We present an analysis on the reflectance and transmittance of unpolarized incidence at various film thickness and complex refractive index for a thin film on a substrate of finite thickness. The contours of constant R and T in the (n_1, k_1), (n_1, d_1) and (k_1, d_1) planes are examined in order to facilitate an optimal combination of experimental measurements for inverse estimation of parameters. R measured at a large angle of incidence, combined with normal T and near normal R are chosen to reduce erroneous solutions or nonconvergence in estimation of parameters. To prevent multiple solutions from the ill-posed problem of the numerical estimation of parameters, an additional measurement of R can be used in computation. In association with the parameter estimation, a least squares method is utilized and simultaneous measurements of spectral complex refractive index and film thickness are performed for a PVA film on a ZnSe substrate. Experimental results are in good agreement with the existing data. In the previous study, the k_1 of a PVA film is estimated lower than the wavelength of 10 μm. And in the present results, the infrared optical constants of a PVA film in the 2.5-21.5 μm wavelength range are determined. The method developed herein may hold considerable promise as a practical technique for determining optical constants and film thickness.

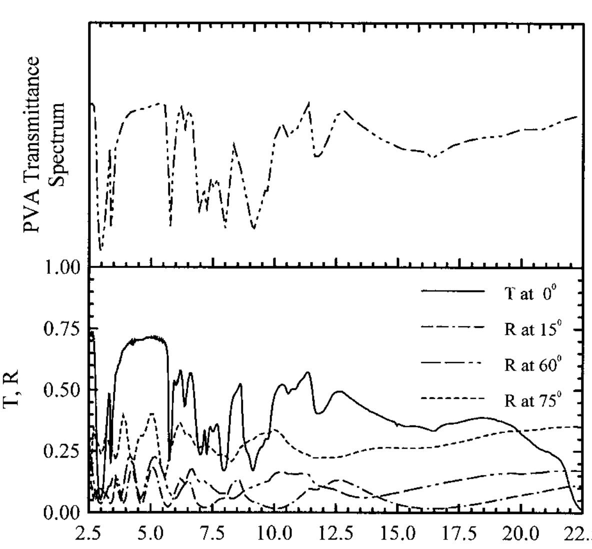

Fig. 9. The spectral dependencies of the normal transmittance and reflectances at three angles of incidence for a PVA film on a substrate of ZnSe.

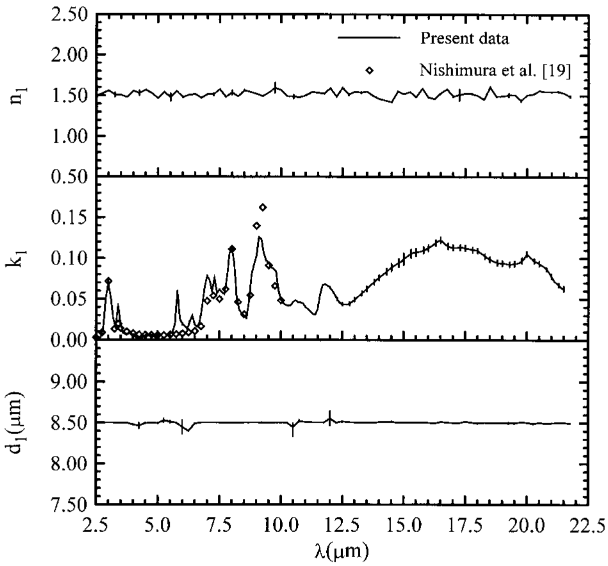

Fig. 10. Optical constants and thickness for a PVA film.

Appendix A.

The analytical expressions for the dependencies of R and T on the real and imaginary parts of the refractive index (n_i and k_i, respectively), the wavelength of incidence λ, the film thickness d_i, the angle of incidence φ_0 are complicated, and are given in terms of the Fresnel reflection and transmission coefficients. Putting the refractive index of air, $n_0 = n_3$, equal to one, we let

$$n_0\cos\varphi_0 = N_0 \quad \text{(A1)}$$

$$\hat{n}_1\cos\hat{\varphi}_1 = u_1 - iv_1$$

$$\hat{n}_2\cos\hat{\varphi}_2 = u_2 - iv_2$$

$$n_3\cos\varphi_3 = N_3$$

The angles φ_0, $\hat{\varphi}_1$, $\hat{\varphi}_2$ and φ_3 are related by Snell's law; we know

$$n_0\sin\varphi_0 = \hat{n}_1\sin\hat{\varphi}_1 = \hat{n}_2\sin\hat{\varphi}_2 = n_3\sin\varphi_3 \quad \text{(A2)}$$

then

$$u_1^2 = \frac{1}{2}\Big\{\big(n_1^2 - k_1^2 - n_0^2\sin^2\varphi_0\big) + \big[4n_1^2k_1^2 + \big(n_1^2 - k_1^2 - n_0^2\sin^2\varphi_0\big)^2\big]^{1/2}\Big\} \quad \text{(A3)}$$

$$v_1^2 = \frac{1}{2}\Big\{-\big(n_1^2 - k_1^2 - n_0^2\sin^2\varphi_0\big) + \big[4n_1^2k_1^2 + \big(n_1^2 - k_1^2 - n_0^2\sin^2\varphi_0\big)^2\big]^{1/2}\Big\} \quad \text{(A4)}$$

$$N_3 = (n_3^2 - n_0^2\sin^2\varphi_0)^{1/2} \quad \text{(A5)}$$

u_2^2 and v_2^2 are expressed as the similar forms to u_1^2 and v_1^2 by exchanging the subscripts. Similarly, we let

$$\frac{n_0}{\cos\varphi_0} = N_0^{'} \quad \text{(A6)}$$

$$\frac{\hat{n}_1}{\cos\hat{\varphi}_1} = u_1^{'} - iv_1^{'}$$

$$\frac{\hat{n}_2}{\cos\hat{\varphi}_2} = u_2^{'} - iv_2^{'}$$

$$\frac{n_3}{\cos\varphi_3} = N_3^{'}$$

then

$$u_1^{'} = \frac{u_1(n_1^2 - k_1^2) + 2n_1k_1v_1}{[4n_1^2k_1^2 + (n_1^2 - k_1^2 - n_0^2\sin^2\varphi_0)^2]^{1/2}} \quad \text{(A7)}$$

$$v_1^{'} = \frac{-v_1(n_1^2 - k_1^2) + 2n_1k_1u_1}{[4n_1^2k_1^2 + (n_1^2 - k_1^2 - n_0^2\sin^2\varphi_0)^2]^{1/2}} \quad \text{(A8)}$$

$u_2^{'}$ and $v_2^{'}$ are expressed by exchanging the subscripts. Then the Fresnel coefficients can be expressed explicitly by the complex refractive indices, the wavelength of incidence, the thicknesses of layers and the angle of incidence. So the reflectance and transmittance can be deduced.

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