熱輻射吸收性薄膜輻射熱性質與厚度之量測與分析

An analysis for Simultaneous Measurement of Spectral Optical Constants and Thickness of an Absorbing Thin Film on a Substrate

計畫編號：NSC89-2212-E-009-022

執行期限：88 **年** 08 **月** 01 **日至** 89 **年** 07 **月** 31 **日**

主持人：**林振德　國立交通大學機械工程學系**

一、　中文摘要

本計畫針對熱輻射吸收性的薄膜被覆在一熱輻射吸收性的基材上,建立理論分析模式和實驗梁測方法，以同時獲得此薄膜的複數行光學折射率和其厚度。計畫中推導出薄膜塗層受一傾斜入射光源照射下,其穿透率和反射率的表示式,並探討不同參數變化(如薄膜或基材的複數型光學折射率、厚度和入射角等)對此穿透率和反射率的影響；進而建議最佳的實驗量測組合，以避免再將實驗量測值作逆運算德蹈光學折射和厚度時，遭遇到多重解的問題，並提升逆運算參數值之精確度。另外，計畫中針對薄膜紅外線光學性質量測建立量測理論，量測方法利用了最小平方誤差法以逆運算得到薄膜在不同頻譜下的複數型光學折射率和其厚度。計畫中並實際以實驗方法運用高分子材質(PVA)**研製薄膜,量測不同角度下薄膜的穿透率和反射率。並應用量測理論進行光學長數及厚度參數之估算，實驗結果和已知文獻中的結果作比較，驗證了本實驗方法和理論計算的正確性，另外此實驗知完成也使得** PVA **之頻譜光學常數之資料更臻完備。**

二、　英文摘要

This project describes a technique and also illustrates an application of the technique for simultaneously measuring both the spectral complex refractive index (n1,k1)and the thickness d1 of an absorbing thin solid layer on a thick substrate. The contours of constant reflectance R and transmittance T in the (n1,k1), (n1,d1) and (k1,d1)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.

三、　計劃緣由及目的

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.

Many methods for the optical analysis of a thin film deposited onto a thick substrate with finite thickness have been published. Most of the previous works included systems which involved an absorbing thin film deposited on a transparent substrate [1-5] or normally incident light [6]. While considering the measurements of both the optical constants and film thickness, they all proposed methods which determine the optical properties and thickness separately.

In this project, we are motivated to accurately determine the optical constants as well as the film thickness of an absorbing thin film on an absorbing substrate. 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 the previous investigations.

四、理論模式

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 β_i, which are contracted in the complex refractive indices $\hat{n}_i=(n_i-k_i)$ and $k_i=\beta_i\lambda/4\pi$. Both the boundaries of two media are ideally flat and smooth. The refractive indices of two ambient media are n_0 and n_3, respectively. This system of thin film/substrate assembly is shown in Figure 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. The detail expression of the reflection and transmission characteristics of the system is described in reference [7].

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. The detail algorithm of the inverse scheme can be seen in reference [7].

五、實驗裝置

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 inversed 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℃ for 6 hours 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 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 spectrum. The spectral dependences 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 $4cm^{-1}$. 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%.

六、結果與討論

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.

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=1000μm. 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. Figure 2 shows such contour plots for the normal reflectances and transmittances, R and T, when the ratio of the thickness of film to wavelength of incident ray, $d(=d_1/\lambda)$, is equal to 0.1. 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 solutions region could be found where k_1 is small. The multiple solutions region also represents the region 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 Figure 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 [8] 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 Figure 2, we notice that the angle of intersection between the R and T curves is small in some regions. Thus, some 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 Figure 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 Figure 3. We also plot in Figure 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 Figure 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 Figure 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 angle 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. Figure 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 Figure 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 Figure 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 to 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 to zero as d is large. It is also illustrated in the figure that the contours (T,R) intersect at more 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 Figure 7, the magnitude of R is only slightly changed with φ_0 as φ_0 increases but increases 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 angle of incidence the reflectance is not sensitive to the absorption index and the effect of 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 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 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. 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 Figure 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 inversion process. It is noticed that there exists a satisfactory coincidence of n_2 and k_2 between our results and existing data [9]. The results of n_2 also agree well with those published by Saito et al. [10] 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 Figure 9, the curve manifests the normal transmittance spectrum to a PVA film as published by previous investigators, while in the lower portion of the figure four different curves respectively illustrate the normal transmittance spectrum and reflectances 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 Figure 8. Using the spectral dependencies of the measurements of PVA-film/ZnSe-substrate system shown in Figure 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. Figure 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 λ=22.0 μm, and the solutions among these bands are difficult to derive because of the numerical difficulty mentioned earlier. In previous investigations [11], 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 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 [11] and present results, especially in the strong absorption bands of 5.8 μm, 6.4 μm and 7.5 μm. In Figure 9, these three absorption peaks can be found in both the present study and work in, but not shown in the results presented by Nishimura et al.. The average thickness of PVA film is 8.521 μm, and the maximum variation in 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.

七、結論

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 k1 of a PVA film is estimated lower than the wavelength of 10μm. And in the present results, the infrared optical constants of a PVA film in the 2.5-21.5μm wavelength range are determined. The method developed herein may hold considerable promise as a practical technique for determining optical constants and film thickness.

八、參考文獻

1. E. Elizalde, F. Ruedam Thin Solid Films 122 (1984) 45.
2. M. Chang, U.J. Gibson, Appl. Opt. 24 (4) (1985) 504.
3. R. Swaenepoel, J. Phys. E: Sci. Instrum. 16 (1983) 1214.
4. M. Kubinyi, N. Benko, A. Grofcsik, W. J. Jones, Thin Solid Films 286 (1996) 164.
5. Y. Wang, M. Miyagi, Appl. Opt. 36 (4) (1997) 877.
6. L. Vriens, W. Rippens, Appl. Opt. 22 (24) (1983) 4105.
7. J. J. Chen, J. D. Lin, L. J. Sheu, Thin Solid Films 354 (1999) 176-186.
8. O. Hunderi, Appl. Opt. 11 (7) (1972) 1572.
9. L. Ward, in: E.D. Palik (Ed.), Handbook of Optical Constants of Solids II, Academic, Boston, 1991, pp. 753.
10. M. Saito, S. Nakamura, M. Miyagi, Appl. Opt. 31 (28) (1992) 6139.
11. M. Nishimura, M. Kuraishi, Y. Bando, Kagaku Kogaku Ronbunshu 9 (2) (1983) 148.

附圖

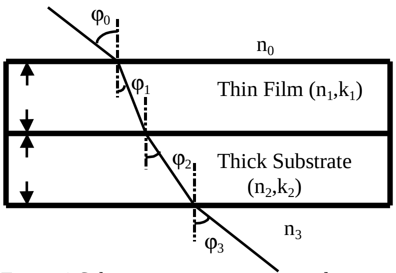

Figure 1 Schematic representation and notation

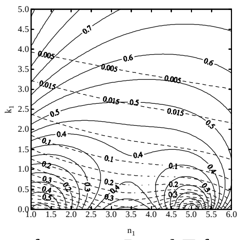

Figure 2 Contours of constant R and T for normal incidence and d=0.1

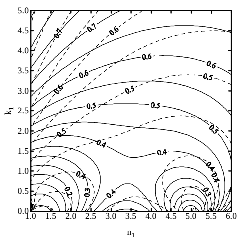

Figure 3 Contours of constant R for 75° angles of incidence and d=0.1

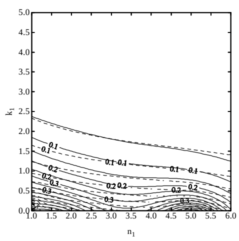

Figure 4 Contours of constant T for 75° angles of incidence and d=0.1

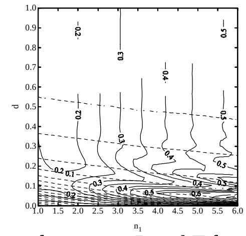

Figure 5 Contours of constants R and T for normal incidence and k_1=1.0

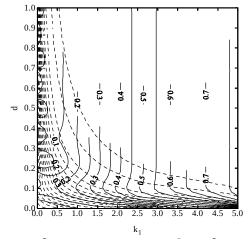

Figure 6 Contours of constant R and T for normal incidence and n_1=2.0

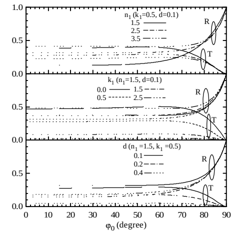

Figure 7 R and T as functions of incident angle φ_0 in degrees

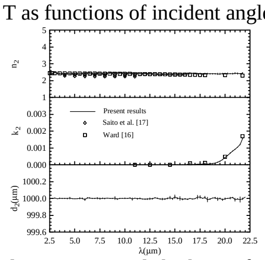

Figure 8 Optical Constants and thickness for a substrate of ZnSe

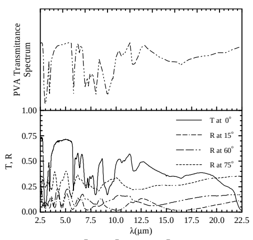

Figure 9 The spectral dependencies of the normal transmittance and reflectances at three angles of incidence for a PVA film on a substrate of ZnSe

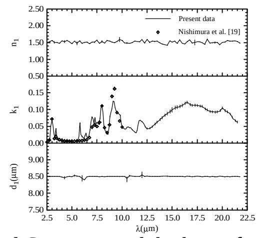

Figure 10 Optical Constants and thickness for a PVA film