Determination and Analysis of the Optical Parameters of Polymer Thin Film based on Spectrum*

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***Abstract*—A method to determine the optical parameters of polymer thin film by use of the transmission spectrum is proposed, with the improved simulated annealing algorithm developed to perform its inverse calculation. A special phenomenon due to the almost equal refractive index between film and substrate, that is, the small waves on spectrum curves which make the information of film thickness losing, has been discussed in detail. Based on the tested transmission spectrums of polymer optical thin films fabricated on K9 glass substrates, the dispersion curve of refractive index in visible band is figured out. Its calculated refractive index in the wavelength of 1547 nm is 1.3933, with the accuracy higher than 0.58% by comparing with the one measured by traditional coupled prism method. The analyzed result shows that the improved algorithm works well, by which the calculated optical parameters can converge to the right values.**

I. INTRODUCTION

It is very important for the optical parameters of thin films to be measured and determined exactly, especially in their preparation, researching and application. Predecessors had put forward various methods for accurate measurement, such as ellipsometric method [1], coupled prism method [2], Abeles method [3] and the like, each of which has their own advantages otherwise disadvantages. There are many benefits for ellipsometers, such as non-destructiveness, high sensitivity and accuracy, particularly for the spectroscopic ellipsometer working at continuous wavelength now. Nevertheless, the shortcomings of periodic problem of thickness, which requires the ideal thickness from 1 nm to 1000 nm, and of the complexity in processing the measured data exist. For coupled prism method, a situation of film refractive index higher than substrate one is required, also with single measured wavelength and difficult preparation. In addition, Abeles method only applies to those general transparent thin films for its visible measuring wavelengths.

Spectrophotometer is an instrument to be used for testing the optical properties of materials, which can accurately scan reflection, transmission and absorption spectrums in a wide wavelength band. Measuring the transmission spectrum is measured with the normal incident light beam, the information about film optical constants and thickness can be acquired through an inverse calculation. The formula used in the calculation, whose derivation based on the electromagnetic field theories is rigorous, has been subjected to the extensive concern of domestic and international scholars [4-6]. There is the virtue in getting higher accuracy, being non-destructiveness and non-restriction in wide wavelength band, but the most difficulty to apply this method is that the evaluation function $\triangle$ is very intricate with the instance of minimum value multiple-peaks in the range of film optical constants and thickness, i.e. n, k, and d. Furthermore, the minimum values are extremely closed to precipitous 'well-wall', for which there exists not a stable numerical algorithm as an effective solution. So in order to implementing the method, it is quite significant to build an optimized model and utilize an improved algorithm with great efficiency and strong searching ability. In this paper, an improved simulated annealing algorithm was developed to solve the evaluation function, and the predigestion of the model was analyzed. Finally, it represents the application of this method to a practical polymer thin film in detail.

II. THEORETICAL BACKGROUND

A. *The formula of transmittance*

The model of reflection and transmission in the layered media comes from the multilayer medium model based on the electromagnetic field [6-7]. In practice, a thin film of uniform coating is formed on a thick substrate using modern micro-nano technology, whose structure can be viewed as a layered media with four parallel interface including air. And for simplicity, we can assume that every layer is homogeneous and isotropic. The refractive index n and extinction coefficient k are both token of basic optical properties of materials, known as optical constants. According to the electromagnetic theory, they can be combined by means of the expression $N = n + ik$. The transmission spectrum method is to find out the relationship between a film spectrum and its optical constants and thickness d, and then to construct a model of inverse calculation. Using the optimized algorithm upon the model, three film optical parameters including n, k and d can be obtained finally.

The reflection and transmission model for a three-layer parallel medium is given in Fig. 1. As the light beam travels from Region 1 through Region 2 to Region 3 at normal incidence, the boundary condition of electromagnetic wave is matched in each interface

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between every two layer. So the electric field amplitudes of those waves reflected and transmitted by the film can be presented by the following expressions, with respective incidence directions, (321) and (123), considered

$$r_{321} = \frac{r_{32} + r_{21}\exp(\mathrm{i}\psi)}{1 + r_{32}r_{21}\exp(\mathrm{i}\psi)} \qquad (1a)$$

$$t_{123} = \frac{t_{12}t_{23}\exp(\mathrm{i}\psi/2)}{1 + r_{12}r_{23}\exp(\mathrm{i}\psi)} \qquad (1b)$$

where r_{ij} and t_{ij} are the Fresnel coefficients of reflection and transmission respectively, while Ψ is the phase difference of the waves between two interfaces and defined by

$$\psi = 4\pi N_2 d / \lambda \qquad (2)$$

$$\mathrm{Re}(\psi) = 4\pi n_2 d / \lambda = \varphi \qquad (3)$$

$$\mathrm{Im}(\psi) = 4\pi k_2 d / \lambda = \alpha d \qquad (4)$$

in which φ is referred to as the phase angle and α is usually called the absorption coefficient of film. Corresponding values of the reflectance and transmittance are defined by

$$R_{321} = r_{321} r_{321}^{*} \qquad (5a)$$

$$T_{123} = (n_3/n_1) t_{123} t_{123}^{*} \qquad (5b)$$

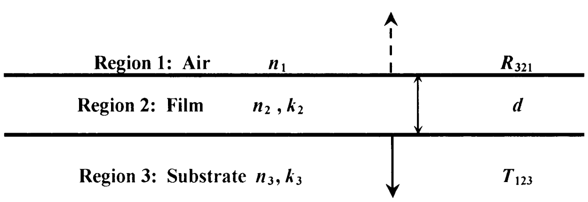

Figure 1. The model of three-layer parallel medium.

For the ideal model of a thin film as shown in Fig. 2, there is one more interface compared to the above model with the air as the last layer of medium. Using the transmission matrix, the total transmittance is obtained as

$$T = \frac{(1-\rho)T_{123}U}{1-\rho R_{321}U^2} \qquad (6)$$

where the factor $\rho = [(n_1 - n_3)^2 + k_3^2] / [(n_1 + n_3)^2 + k_3^2]$ is the reflectivity of 1-3 interface. Any absorption in the substrate is taken into account by the factor U, which can be determined by the following formulas

$$T_s = \frac{(1-\rho)^2\exp(-\alpha_3 d_3)}{1-\rho^2\exp(-2\alpha_3 d_3)} \qquad (7)$$

$$U^{-1} = \frac{(1-\rho)^2}{2T_s} + \left[\frac{(1-\rho)^4}{4T_s^2} + \rho^2\right]^{1/2} \qquad (8)$$

in which T_s represents the transmittance of a bared substrate. For a transparent substrate, $k_3 = 0$, and thus $U = 1$. At this position, Eq. (7) becomes

$$T_s = \frac{2n_3/n_1}{1+(n_3/n_1)^2} \qquad (9)$$

Substituting R_{321} and T_{123} from Eq. (5) into Eq. (6), one gets for the transmittance formula [6] as follows

$$T = \frac{A\exp(\alpha d)}{B\exp(2\alpha d) + C\exp(\alpha d) + D} \qquad (10)$$

where four parameters are supposed as

$A = 16n_3(1-\rho)(n_2^2 + k_2^2)U$
$B = st - Usv\rho$
$C = [2(4n_3k_2^2 - ZY)\cos\varphi + 4k_2(n_3Y + Z)\sin\varphi] - \rho U^2[(4k_2(Z - n_3Y)\sin\varphi - 2(ZY + 4n_3k_2^2)\cos\varphi)$,
$D = uv - U^2tu\rho$

in which $u = (n_1 - n_2)^2 + k_2^2$, $v = (n_2 - n_3)^2 + k_2^2$, $s = (n_1 + n_2)^2 + k_2^2$, $t = (n_2 + n_3)^2 + k_2^2$, $Y = n_2^2 - n_1^2 + k_2^2$ and $Z = n_2^2 - n_3^2 + k_2^2$.

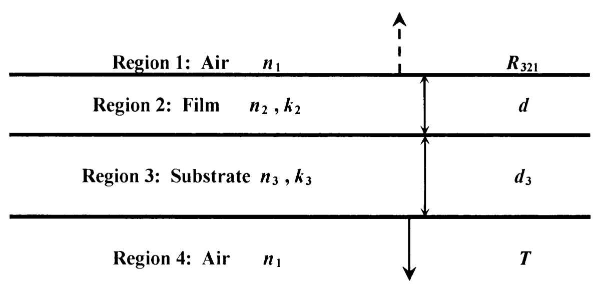

Figure 2. The model of four-layer parallel medium.

As a result, we can retrieve the transmission spectrum of a thin film at normal incidence of light wave with the wavelength designated as in Eq. (4) for the variable α in Eq. (10).

B. Determination of Optical Parameters

The inverse calculation based on the transmission spectrum method builds upon the construction of the evaluation function. As a function on the wavelength λ with three unknown parameters of n_2、k_2 and d, the transmittance formula can be written as $T(\lambda, n_2(\lambda), k_2(\lambda), d)$. The measured transmittance by spectrophotometer is represented as $T_m(\lambda)$, and the calculated one through formula (10) as $T_s(\lambda, n_2(\lambda), k_2(\lambda), d)$. When the later value equals to the former, that group of calculated parameters $(n_2(\lambda), k_2(\lambda), d)$ is the right information of thin film to be desired. The evaluation function is constructed using least square method as follows

$$\Delta = \sum_{\lambda}[T_s(\lambda; n(\lambda), k(\lambda), d) - T_m(\lambda)]^2 \qquad (11)$$

Focusing on finding the minimum of function $\triangle$, that means T_s approaches T_m at a close range, the corresponding group of parameters ($n_2(\lambda)$, $k_2(\lambda)$, d) can be regarded as the true parameters of thin film.

As there exists lots of minimal values in the range of ($n_2(\lambda)$, $k_2(\lambda)$, d), the formula of $\triangle$ turns out to be too complex to be solved. Various techniques have been researched to find the minimum, such as the most universal approaching method, and also steepest descent algorithm, conjugate gradient algorithm, Newton algorithm and so on. But unlike these methods with difficulty to fit the complexity of formula $\triangle$, some intelligent optimization algorithms in the domain of programming the engineering model can be brought in to solve the problem. It has been proved to be of excellent abilities for numerical inverse calculation, including genetic algorithm, ant colony algorithm, simplex algorithm and simulated annealing algorithm, etc..

The simulated annealing algorithm is an excellent global algorithm, with characteristics like efficiency, haleness and initial value independence and having been applied to the transmission spectrum method by some domestic researchers [4]. In the procedure, the evaluation function is designated to be the energy in the course of annealing, and those parameters ($n_2(\lambda)$, $k_2(\lambda)$, d) of thin film simulate the state of molecular thermodynamic movement.

However, what must be emphasized that, the result by this algorithm tends to plunge into the local minimum and hard to dap out, due to the precipitous 'well-wall' and the close approaching between minimal values and the real minimum of $\triangle$. Moreover, a defect exists that the minimal value ever searched cannot be remembered during the execution process. So even with a set of proper cooling schedule, the satisfied solution of this problem is still hard to be reached. Some improvement and variation are adopted, mainly embodying hereinafter:

(1) Tempering and annealing method. Temper means the temperature rises, which results in an increasing acceptance probability and will benefit bouncing out the trap of local minimum. Then, the process of annealing continues to renewedly search the minimum at another state.

(2) Algorithm with memory. Although the algorithm itself can ideally converge and get the global minimum in the end, the numerical experiment shows it is not like that. So a string of memory-function code is added to remember the smallest minimal values ever searched, for which a comparison will be done to select the smaller as the searching result.

Meanwhile, at the end of the algorithm, a local search will activate to be sure to reach the 'well-bottom' around the result returned by the algorithm.

III. Analysis for a Special Phenomenon

The transmission spectrum of a piece of K9 glass substrate, which is common in lab, was measured by Tu-1901 UV-VIS spectrophotometer, as shown in Fig. 3. The substrate is transparent so that $k_3 = 0$ and Eq. (9) is right the formula for the transmittance of bared substrate.

For PDMS (polydimethylsiloxane) as the studied polymer thin film, it should be noticed that its refractive index of $n_2 = 1.4014$, measured at 1547 nm by coupled prism method, approaches the index of the glass substrate [9]. It has to be discussed that the relationship between the transmittance formulae of thin film and bared substrate when $n_2 \approx n_3$.

Substituting $k_2 = 0$ and $n_2 \approx n_3$ into Eq. (10), one can get Eq. (9) after a straightforward calculation. From the aspect of physical meaning, the coating material of the thin film turns to be the same substance as the substrate when the indices are equal. Thus, the total transmittance definitely equals to that of bared substrate.

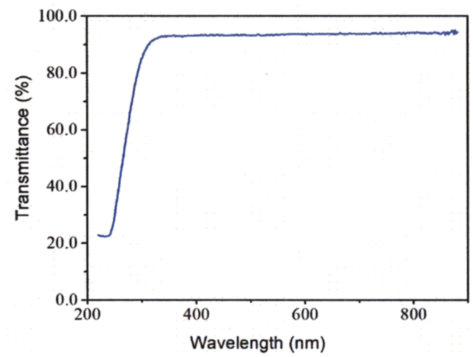

Figure 3. The measured transmission spectrum for bared K9 glass substrate.

The above phenomenon is studied through the transmission spectrum drawing with MATLAB. The dispersion formula of the refractive index for K9 glass substrate is given as [10]

$$n_3^2(\lambda) = A_0 + A_1\lambda^2 + A_2\lambda^{-2} + A_3\lambda^{-4} + A_4\lambda^{-6} + A_5\lambda^{-8} \quad (12)$$

where A_0, A_1, A_2, A_3, A_4 and A_5 respectively are constants with values of 2.25586, 2.80146e-3, 1.69657e-2, -1.11452e-3, 1.26044e-4 and -4.83488e-6, and the wavelength in Eq. (12) is expressed in microns. For the situation of $k_2 = 0$ and $n_2 \approx n_3$, the transmission spectrum of thin film was drawn in Fig. 4, ignoring the ultraviolet band as in Fig. 3. It shows a sharp absorption and belongs to the case of abnormal dispersion, with only the visible band of 400 ~ 850 nm considered.

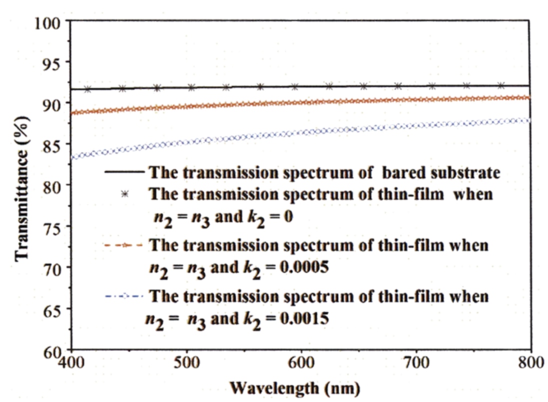

Figure 4. The transmission spectrum for thin film when $n_2 = n_3$.

The solid line and the '*' line in the figure overlap each other, which indicates again that the transmission spectrum of thin film can be identified with the one of K9 glass substrate. And while making a comparison among the curves of $k_2 = 0$、$k_2 = 0.0005$ and $k_2 = 0.0015$, a rule can be found that the curve of the film transmission spectrum is affected by k_2 and the effect varies at different wavelengths. So one can judge that $k_2 = 0$ when the curve of the film spectrum is parallel with that of substrate.

IV. TREATMENT OF PDMS THIN FILM

A. Calculation of Optical Constants

The measured transmission spectrum of PDMS thin film is given in Fig. 6, which indicates that $k_2 = 0$ and the visible band of 400~850 nm is considered.

The dispersion relationship as a function of wavelength cannot be overlooked when finding the film optical constants at a given wave band. But if the band is smaller enough, the dispersion can be ignored that will not make an impact on the transmittance calculation. Improving the simulated annealing algorithm and assuming the equal indices at three wavelength points nearby a center wavelength, the film index n_2 at the center wavelength can be found through the inverse calculation. In the inverse calculation, three groups of transmittance data are taken into the evaluation function $\triangle$ to obtain two parameters, n_2 and d simultaneously. After certain amount of n_2 obtained, a dispersion formula is utilized to fit the dispersion curve of n_2 in the whole wave band. In Table 1, three groups of data for the inverse calculation of PDMS thin film are listed.

Theoretically, the found set of parameters which makes the evaluation function $\triangle$ to be the least is just the solution we need. As long as the fifth effective bit of T_s calculated can round to make the same as the four effective bits of T_m, due to the precision of spectrophotometer, it can be thought that the true solutions have been found out. Some similar solutions had been searched by the improved simulated annealing algorithm and when they are substituted into Eq. (10) to calculate the transmittance, the results all turn out to be the same as those measured data. Furthermore, the values of evaluation function found by these true solutions are very close to each. The numerical simulation indicates that the improvement of simulated annealing algorithm is effective for searching the minimal value.

TABLE 1. DATA OF INVERSE CALCULATION FOR PDMS THIN FILM

Center wavelength (nm)		512			764			816		
n_3		1.5202			1.5113			1.5103		
Transmittance	λ (nm)	514	512	510	766	764	762	818	816	814
	T_m (%)	93.08	93.10	93.06	93.78	93.76	93.74	94.12	94.10	94.06
n_2		1.4637			1.4290			1.4082		
d (nm)		1488.7			1480.0			1322.5		

B. Analysis and Discussion

The Cauchy equation is a common formula, widely used for describing the dispersion of material refractive index without any physical meanings [11]. Using its first two terms to fit the refractive indices obtained by the inverse calculation, the dispersion expression of PDMS film is given as

$$n_2(\lambda) = 1.3845 + 20983.60845/\lambda^2 \qquad (13)$$

the curve of which is drawn in Fig. 5, the calculated refractive index n_2 from this curve is 1.3933 at 1547 nm, which is near to the value of 1.4014 measured by the traditional coupled prism method [9]. Thus, the calculation accuracy is up to higher than 0.58%.

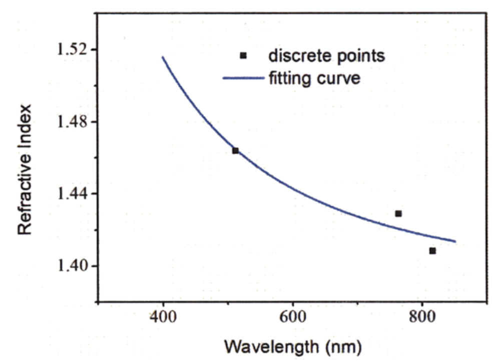

Figure 5. The calculated refraction indices of PDMS thin film vs wavelength.

Three values of the thickness given in Table 1 are averaged to be as the practical thickness of PDMS thin film. So the found film thickness is 1430.4 nm, near to the observed results by the surface profilometer and SEM picture. Substituting the corresponding optical parameters into Eq. (10), the transmission spectrum among the band of 400 ~ 850 nm can be retrieved.

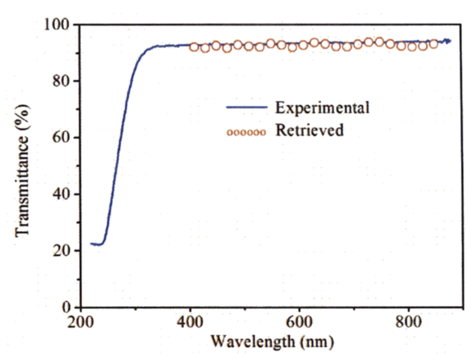

Figure 6. The transmission spectrum of PDMS thin film.

As shown in Fig. 6, the variation trend of the retrieved transmission spectrum is almost identical with the measured one, but with some kind of specific 'wave' existing. In other words, the thickness information of thin film is easily lost during the measurement and data process by fitting and smoothing technology. According to Eq. (10), the 'waves' number on the spectrum retrieved, which is just like a beeline because of the very small amplitude of 'waves', will decrease for the thickness of $d <$ 1430.4 nm. Conversely, the 'waves' number will increase for $d <$ 1430.4 nm. While the spectrum will be taken as a beeline, because the amplitude of 'waves' is so small that they can be considered as noises added into the mean level measured.

V. CONCLUSION

In this paper, an improved simulated annealing algorithm is put forward based on the transmission spectrum method to performing the inverse calculation for polymer thin films. It is proved that the minimum value of evaluation function $\triangle$ can be searched efficiently and rapidly. And a special situation is studied and discussed, that is the information of film thickness losing in the measured spectrum due to the very approaching between the minimum value and small amplitude of 'waves'. The calculation results show that the accuracy higher than 0.58% for refractive index can be acquired, while the value of thickness could be just a reference.

Furthermore, the phenomenon of abnormal dispersion existed in the wave band is studied, which means there is a sharp absorption in the thin film. So the optical constants and thickness of PDMS thin film are determined firstly in the wave band of normal dispersion, and then a subtractive Kramers-Kronig method is brought into the calculation of all optical constants in entire wave band, including the sharp-absorption region. The analyzed results indicate that the expressions of film optical constants can be fitted well.

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