

Nondestructive determination for the thickness of spin-coated polymer films by transparent coefficient

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Polymer films thickness is one of the critical factors for the operation performance of the integrated optical devices (IODs) based on polymer planar waveguides and it is difficult to real-time determine it during corresponding fabrication process. A variety of approaches, which have been presented before, are either of less precision or more contamination of the film surfaces. In this paper a practical method, in which the absorbance of the polymer film using Lambert law to determine the thickness of spin-coated polymer films, was presented. Compared with other methods, it can get an acceptable accuracy without using specialized and expensive instruments, and the surface of the film with not be contaminated during the measurement process. The experimental results compared with other methods were listed and depicted in confirming our method's availability. The factors that may have influence on the employment of our method were analyzed and discussed.

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Being of higher second- and third-order optical-electronic coefficients, greater nonlinear effect and tractability contrasted with inorganic materials, polymer was widely used in the development of integrated optical devices (IODs) during the current years. Of all parameters describing polymer film properties and characteristics, thickness is the critical one having great influence on the performance of developed IOD based on these films. Spin coating is a common way to form a thin uniform polymer film on certain substrate for this development^[1]. Being intrinsic, the thickness of spin-coated polymer films could not be real-time controlled during its fabricating process and just could be determined or predicted after the process accomplished. So it is still a promising field to seek for a more effective method for the determination of the thickness of spin-coated polymer films. To our knowledge, a large variety of methods for the determination of spin-coated polymer films thickness exist, each with its own benefits and disadvantages^[2-7]. These methods can roughly be divided into two categories: direct and indirect measurements. Direct measurement means measuring film thickness directly with specialized equipments such as prism coupler, tallstep and almost giving quite accurate data. The main disadvantages of the direct measurement are the use of expensive instruments, the need of very flat surfaces, and it is almost unavoidable for these methods that the instrument sensor often touches so closely with the films that the surfaces are destructed. Indirect measurement covers m-lines method, micro-weight method, and a lot of mathematic-model ways, which are based on the employment of spinning-velocity, concentration of polymer solution or other physics parameters of the films, and predict the thickness according to corresponding rationale while the environment temperature, kinds of solvent and other environment factors have great influence on the final results^[1,4,5,7]. In the interest of overcoming these disadvantages of both direct and indirect measurements, especially to avoid damaging or befouling film surface, we attempted to develop a special indirect measurement by using the transparent coefficient based on Lambert law. By this way, no ex-

pensive specialized instruments but a spectrophotometer was needed and environmental conditions had little influence on the final results, and closely touching between the sensor components of the measuring instruments and film surface was avoided. So it was of possibility that damage or contamination to the films surface can be avoided while satisfied accuracy of calculated thickness was gotten.

Lambert law tells us that when a light beam strikes on the surface of a certain nearly transparent material film vertically, if only absorption contribution to the intensity declination is concerned, absorbance of this material (written as β in the following text), which is a physical constant for a certain material, thickness of the film (written as h), and transparent ratio (written as η) obey the relation:

$$I = I_0 \exp(-\beta h), \quad (1)$$

where I denotes the permeation light intensity, I_0 denotes the incident light intensity, I/I_0 denotes the pure transparent ratio of a certain film. Thus, knowing two of the three parameters η , h , and β , the third one can be easily determined by solving Eq. (1). But as shown in Table 1, the values of β , which were directly calculated according to Eq. (1) based on measured transparent coefficient and h , had a great dispersion for a group of films, which were just with different thickness but fabricated under the nearly same conditions. These differences were greatly out of the margins of experimental errors and contradicted the essential physics principle, that the absorbance for a certain material is constant. This was analyzed as that the factors causing the attenuation of light intensity had two parts — absorption contribution, which is directly related with the films thickness and obeys Lambert law, and non-absorption contribution (written as Δ in the following text) including a little contribution of reflection on the surface, scattering, which almost have nothing to do with the films thickness. Actually, the transparent ratio measured by using a spectrophotometer (written as Σ) includes two parts — η and Δ . It was η with h and β that obeys Lambert law, not Σ .

So directly using Lambert law to determine h based on β and Σ by solving Eq. (1) will not get correct results. We must find and subtract Δ from Σ .

In terms to find the value of Δ for each polymer film, an assumption that Δ of every film is the same and only depends on the films fabrication conditions such as solvent, environment temperature, baking time, and oven temperature, was made as the special strongpoint of our approach. Thus, for two films fabricated under the same conditions as described previously, equations listed below may be deduced:

$$\Sigma_1 = \eta_1 - \Delta_1, \quad (2)$$

$$\Sigma_2 = \eta_2 - \Delta_2, \quad (3)$$

$$\Delta_1 = \Delta_2 = \Delta, \quad (4)$$

$$\eta_1 = \Sigma_1 + \Delta = \exp(-\beta h_1), \quad (5)$$

$$\eta_2 = \Sigma_2 + \Delta = \exp(-\beta h_2), \quad (6)$$

$$\eta_1 - \eta_2 = \Sigma_1 - \Sigma_2 = \exp(-\beta h_1) - \exp(-\beta h_2), \quad (7)$$

$$\exp(-\beta h) = 1 + (-\beta h) + (-\beta h)^2 + \dots, \quad (8)$$

$$\Sigma_1 - \Sigma_2 = (\beta h_1)^2 - (\beta h_2)^2 - (\beta h_1 - \beta h_2). \quad (9)$$

The subscripts 1, 2 refer to the concerning two films. As shown in Eq. (8), for the convenience of calculation, the function $\exp(-\beta h)$ in the Eq. (7) was expanded in a Taylor progression about $(\beta h) = 0$ and only the leading three items—1, $(-\beta h)$, and $(-\beta h)^2$ were kept, thus Eq. (9) was gotten. This simplification will be discussed and proved to have little influence on the accuracy of final results in the next.

Given that the aforementioned assumption is true, for a group of films containing N pieces of spin-coated polymer films, the number of $N \times (N - 1)/2$ algebraic equations alike Eq. (9) may be acquired. By solving these equations, the approximately same values of β and Δ should be calculated by using the measured values of Σ and h . Furthermore, the thickness of other films fabricated under the same conditions could be reversely determined according to the calculated β , Δ , and measured Σ by means of Lambert law again, expressed as Eq. (5) or (6).

To test whether the assumption was correct, by using KW-4A spin coater and processing under nearly

same conditions, two groups of sample films were fabricated, with each group containing six slips of spin-coated PMMA and PMMA/DR1 films, respectively. Their thickness and transparent coefficient were measured by using AM-BIOS-XP-2 tallstep, WFZ-25A spectrophotometer at the wavelength of 890 nm. At this wavelength, transparent coefficient of PMMA and PMMA/DR1 spin-coated films is more than 90% and ensures $(\beta h) \ll 1$, Taylor's series requirement. Then for each group, 15 equations alike Eq. (9) were established. After solving these two groups of equations, the results were calculated and listed in Tables 2 and 3. The dispersion and corresponding trend line of calculated β versus the thickness-difference of the two films were illustrated in Figs. 1 and 2, respectively. From Tables 2 and 3, a conclusion, that for per group of sample films the values of β were almost the same, could be drawn. This showed agreement with the essential physics principle, that absorbance is a constant for a certain material, and demonstrated that the assumption about Δ presented before was correct. Then the value of Δ also can be determined according to measured h and calculated β by employing Eq. (5) or (6). An inspection of Figs. 1 and 2 showed that the more the thickness-difference was, the more accurate the calculated values of β were, accordingly the accuracy of calculated Δ being improved, too.

By now, the essential result of our method, spin-coated polymer films Δ was a parameter just depending on the fabrication conditions, i.e., a constant for spin-coated polymer films fabricated under certain conditions, could be drawn. Additionally, absorbance of certain material also is a physics constant. So our method of determination for the thickness of spin-coated polymer films may be expressed as below: if the Δ and β of certain polymer films made under certain conditions were known in

Table 1. Direct Determination for β with $\lambda = 890$ nm

No.	Σ (%)	Measured h	Calculated β
1	93.93	4.21	14874.205
2	94.04	3.78	16256.615
3	94.24	3.22	18424.07
4	94.40	2.69	21423.476
5	94.58	2.12	26284.994
6	94.73	1.65	32811.808

Table 2. Calculated Results for Group 1

No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
$h_2 - h_1$ (μm)	0.43	0.99	1.52	2.09	2.56	0.56	1.09	1.66	2.13	0.53	1.1	1.57	0.57	1.04	0.47
$(h_2 - h_1)/h_2$	0.102	0.24	0.36	0.5	0.61	0.15	0.29	0.44	0.56	0.16	0.34	0.49	0.21	0.39	0.22
β	2584	3168	3125	3141	3154	3617	3338	3284	3268	3046	3116	3145	3182	3195	3211
$\beta - \bar{\beta}$	-588	-3.6	-47	-31	-18	445	166	112	96.4	-126	-56	-27	10.4	23.4	39.4

$h_2 - h_1$: difference of thickness of two films related by Eq. (9).

$(h_2 - h_1)/h_2$: relative difference of thickness of two films related by Eq. (9); $\bar{\beta}$: average of β

Table 3. Calculated Results for Group 2

No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
$h_2 - h_1$ (μm)	0.78	1.45	1.93	2.25	2.44	0.67	1.16	1.48	1.66	0.48	0.8	0.99	0.32	0.5	0.34
$(h_2 - h_1)/h_2$	0.18	0.33	0.44	0.51	0.56	0.18	0.32	0.41	0.46	0.16	0.27	0.34	0.13	0.21	0.16
β	3370	3217	3257	3217	3219	3090	3182	3138	3150	3377	3217	3223	2976	3076	2980
$\beta - \bar{\beta}$	191	37.7	77.7	37.7	39.7	-89	2.73	-41	-29	198	37.7	43.7	-203	-103	-199

Table 4. Calculated Results and Comparison of Group 1 with $\lambda = 890$ nm

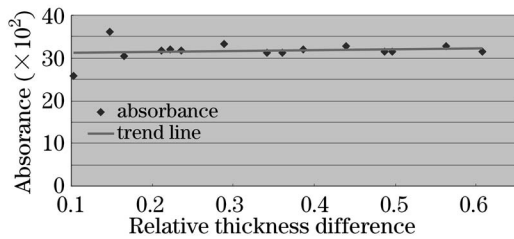
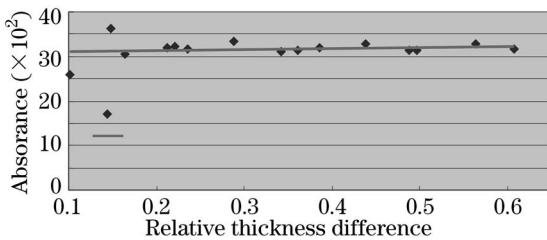
No.	Σ (%)	Measured h	Δ (%)	$\bar{\beta}$	Calculated h	Relative Error (%)
1	93.93	4.21			4.186	-0.570
2	94.04	3.78			3.835	1.455
3	94.24	3.22	4.751	3172.0	3.197	-0.714
4	94.40	2.69			2.688	-0.074
5	94.58	2.12			2.116	-0.189
6	94.73	1.65			1.64	-0.606

Table 5. Calculated Results and Comparison of Group 2 with $\lambda = 890$ nm

No.	Σ (%)	Measured h	Δ (%)	$\bar{\beta}$	Calculated h	Relative Error (%)
1	93.718	4.388			4.421	0.756
2	93.976	3.612			3.599	-0.347
3	94.180	2.935	4.886	3180	2.951	0.553
4	94.341	2.454			2.441	-0.547
5	94.435	2.136			2.143	0.319
6	94.495	1.950			1.953	0.149

Table 6. Influence of Items Number in the Series for Group 1

Kept Items Number	2	3	4
Calculated Value of β	3172.1	3171.85	3171.886

Fig. 1. β versus relative thickness difference of group 1.Fig. 2. β versus relative thickness difference of group 2.

advance, which could be calculated along with the procedure as mentioned earlier, the thickness of other polymer films made of the same material under the same conditions could be determined according to Eq. (5) or (6) by using Σ , Δ , and β . To confirm the validity of our method, the thickness of each film in the same two groups of spin-coated films was calculated by means of our method and the comparison with those measured by using other methods was listed together in Tables 4 and 5. From these tables, a conclusion can obviously be drawn that with the implement of Δ and the average of calculated values of β in place of the actual absorbance, which is really difficult to achieve for some polymer, into Eq. (5) or (6), the determination for the films thickness could get acceptable accurate results.

Additionally, Table 6 showed that keeping three items in Eq. (8) was enough to ensure the accuracy of cal-

culated β , Δ and then the determination for thickness. Increasing this number hardly did well in improving effect.

In conclusion, nondestructive determination for the thickness of spin-coated polymer films by applying Lambert law based on β , Δ , and Σ is doable and practical. Compared with other widely held methods, this method was of high availability, accuracy and concision without the need of expensive equipments, demanding flat surfaces of films, and avoiding the contamination or damage on film surfaces. Expanding the function $\exp(-\beta h)$ as a Taylor's series and only holding the fore three items simplified the mathematic processing and remained accuracy little changed. But in the process of our determination for β and Δ , the thickness difference of the two concerning films should be big enough to ensure the corresponding calculation result's accuracy. Finally, what must be emphasized was that to ensure the reliability and accuracy of our method, the fabrication conditions of films should be strictly controlled to be as consistent as possible with the corresponding piece of films used for the determination for β and Δ . This was essential fundament for presented method in this paper.

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