

ERROR ARISING FROM ORIGINAL APPROXIMATION IN PHOTOTHERMAL
MEASUREMENT OF WEAK ABSORPTION OF OPTICAL THIN FILM

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INTRODUCTION

The technique of photothermal deflection spectroscopy (PTDS) for absorption measurement of optical thin film is simple in installation and fast in detection. However, while measurable absorbance reaches the order of magnitude of 10^{-7} , e.g. in studies of optical thin film and investigation of laser damage mechanisms [1,2], we are still doubtful of its precision because of the lack of independent evaluation with available instruments whose precision could reach this lower limit. This work aims at giving a theoretical investigation on the source of error in order to obtain a realistic estimate of measurement error and hence to find optimal way to minimize measurement error in applying PTDS to optical thin film.

THE PRINCIPLE OF PTDS MEASUREMENT

The technique of PTDS is schematically shown in Fig.1. A laser beam (the pumping beam) of power P , which is chopped at a frequency f , is incident vertically on the surface of an optical thin film whose absorbance is to be measured. To measure weak absorption of the film on a transparent

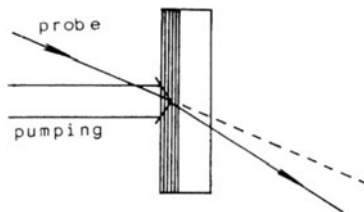


Figure 1. Photothermal effect in an optical thin film

substrate, a probe beam, initially incident at a finite angle ($< 90^\circ$) to the illuminated spot, is detected for its deflection after passing through the film-substrate. The deflection results from an alternating field of refractive indexes in the neighbouring air and the substrate owing to periodic heat flow in the alternating temperature field set up by photothermal (PT) effect in the thin film. This method is transmission detection. Theoretical studies shows that the deflected angle is proportional to the absorbed power from the pumping beam. The deflection then transduces to a potential difference ΔV between the outputs of a double quadrant detector. The deflection voltage is hence proportional to the film absorption, while depending on the incident power measured by a optical voltage V . We have

$$\Delta V = (1/R) \cdot V \cdot A \tag{1}$$

where $1/R$ is a proportional constant and A the absorbance. Calibration of R is made by using carbon-black thin film on the same substrate. The absorbance of the carbon-black film can be obtained using ordinary method with a fractional error less than 3% owing to its strong absorption.

ERROR ANALYSIS

Based on Eq.(1), the fractional error of the measured absorbance is

$$dA/A = dR/R - dV/V + d(\Delta V)/\Delta V \tag{2}$$

where dR/R is the calibration error and the last two terms on the right hand side are the measurement errors from instruments and readings. As shown in the following discussion, dR/R is about 6.96% and the measurement errors about 1.1%. These give total fractional error of 8.06%. Hence, it is unrealistic to claim that PTDS is highly precise and highly sensitive. However, detailed study shows that Eq.(1) comes from a theoretical treatment with basic approximations of PTDS, which brings discrepancy between the true value and the measured one. This generates an intrinsic error to experimental results, the error arising from the theory. Obviously, it cannot be ignored in the measurement of multilayer optical thin film.

THE ERROR ARISING FROM ORIGINAL APPROXIMATION

PTDS measurement of an optical thin film on a transparent substrate as shown in Fig.1 can be simulated as a multilayer medium system (Fig.2). Among medium layers O, I, II, \dots, N , the O is air, the N is the substrate and all others are layers of the optical thin film. The corresponding interfaces are $0, 1, 2, \dots, n$ and the i th layer is sandwiched between the interfaces $i-1$ and i . The temperature distributions of each layer is obtained through solving the heat conduction equation [3]. For simplicity, assume that only the M th layer absorbs. Cylindrical coordinates are used to match the symmetry of the pumping beam: x is the propagation direction

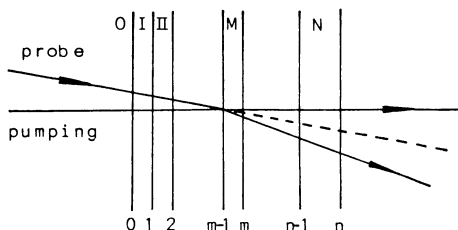


Figure 2. Photothermal effect in a multilayer system

and r the radial variable on the cross section of the beam. The temperature distribution function is expressed in amplitude function A_i and B_i

$$T_i = \int \left[\Gamma(\delta) \cdot \exp(\sigma_i x) \cdot \Delta_{im} + A_i(\delta) \cdot \exp(-\sigma_i x) + B_i(\delta) \cdot \exp(\sigma_i x) \right] \delta \cdot h_0(\delta) \cdot J_0(\delta r) \cdot d\delta \quad (3)$$

where $i = 0, 1, 2, \dots, m, \dots, N$; $\Delta_{im} = 0$ if $i \neq m$ and 1 if $i = m$; σ_i are the heat wave numbers; δ is space frequency in the Hankel transforms of the heat-source term due to absorption, $\Gamma(\delta) = \beta_m I_m / [\kappa_m (\beta_m^2 - \sigma_m^2)]$ (β_m are the absorption coefficients, I the intensity and κ the heat conductivity); $h_0(\delta) = (1/\pi^2) x \cdot \exp[-(\delta w)^2/2]$, (w is radius of light spot of the pumping laser on the M layer). In the transmission detection, the temperature distribution in the substrate is important and its amplitude functions are obtained through propagation calculations of the interface matrices [3]. The very thin thickness of the optical film makes approximations possible:

$$\exp(\pm \sigma_i l_i) \cong 1 \pm \sigma_i l_i$$

since $|\sigma_i l_i| \ll 1$ within the effective range of the space frequency from $\delta = 0$ (intensity I_0) to $\delta = \delta_{\max} = 2\sqrt{2}/w$ (i.e. $I = I_0/e$); and $1 - \exp(-\beta_m l_m) \cong \beta_m l_m$ for weak absorption. The amplitude function A_n of the substrate is derived as follows

$$A_n(\delta) = \beta_m l_m / (\kappa_0 \sigma_0 + \kappa_n \sigma_n) \quad (4)$$

in which we neglect a term of $\Delta f'$ ($\ll A_n(\delta)$). The neglect of term $\Delta f'$ is named 'approximation of thin film'. The $\Delta f'$ term is

$$\Delta f' = [1/(\kappa_0 \sigma_0 + \kappa_n \sigma_n)] \times \left\{ \sum_{i=1}^n \frac{l_i}{\kappa_i} \beta_m l_m + (\beta_m l_m)^2 - \frac{1}{|\Gamma|} \left[\sum_{i=1}^{n-1} \frac{l_i}{\kappa_i} + \sum_{i=1}^{n-1} \kappa_i \sigma_i^2 l_i / \kappa_0 \sigma_0 \kappa_n \sigma_n \right] \beta_m l_m \right\} \quad (5)$$

On the other hand, based on boundary conditions

$$B_n(\delta) = 0. \quad (6)$$

Substituting Eqs.(5) and (6) to Eq.(3), we have the temperature distribution in the substrate due to the optical absorption of the thin film

$$T_n(r, x) = I_m \beta_m l_m \int \frac{\exp(-\sigma_0 x)}{\kappa_0 \sigma_0 + \kappa_n \sigma_n} \cdot \delta \cdot h_0(\delta) \cdot J_0(\delta r) \cdot dr. \quad (7)$$

The alternating temperature field causes a deflection angle [4]

$$\Phi(L') = \frac{1}{n_0} \cdot \frac{\partial n}{\partial T} \cdot \int_{L'} \nabla_{\perp} T(x, t) \cdot dS \quad (8)$$

where L' is the transmission path, n_0 is the average refractive index of the substrate and ∇T is the temperature gradient (\perp for the direction vertical to the propagation direction). Let (y_0, z_0) be the probe beam center on the substrate-air interface, ω_0 be the waist radius of the probe beam, (ξ, η) be the plane coordinate of the double quadrant detector and $PW_{\text{abs}} = I_m \beta_m l_m$. The deflection voltage is then expressed as follows

$$\Delta V = \frac{8V}{\pi w} \int_{-\infty}^{\infty} \exp(-2\eta/w^2) \cdot \Phi(y_0, z_0 + \omega_0 \eta r/w) \cdot d\eta \cdot PW_{\text{abs}}. \quad (9)$$

The factor in front of PW_{abs} is defined as the photothermal response function TH which is readily seen as the function of parameter of the substrate b_n , parameter b_0 of the substrate-air correlation, the spot radius w of the

pumping beam, the waist ω_0 of the probe beam, beam path L, the substrate refractive index n_0 and the refractive index gradient $\partial n/\partial T$ etc. Hence, a simplified expression of ΔV is obtained as follows

$$\Delta V = V \cdot TH(\omega_0, w, b_0, b_n, L, n_0, \partial n/\partial T) \cdot PW_{abs} \quad (10)$$

which is just another form of the Eq.(1).

The derivation shows that Eq.(1) comes with the approximation of thin film in which $\Delta f'$ is neglected. An intrinsic error arises and it is estimated from the ratio

$$\Delta A_n(\delta)/A_n(\delta) = \Delta f'/\beta_m l_m \quad (11)$$

The maximum (i.e. $\delta=\delta_{max}$) intrinsic errors for various optical thin film are shown in the Table 1.

For multilayer thin film, the error is the summation of those due to each layer while the signal is also the summation of those due to absorption of each layer. Hence, the total fractional error is the average of those of each layer. It can be estimated as follows [5]

$$\Delta A_n/A_n = \sum_{i=1}^{n-1} (\kappa_i/\kappa_b)(2\sqrt{2} \cdot l_i/w) \leq (\kappa_{max}/\kappa_b)(2\sqrt{2} \cdot L/w) \quad (12)$$

where L is the total thickness of the multilayer film and κ_{max} is the maximum conductivity among layers. The larger the conductivity is and the thicker the film becomes, the larger the intrinsic error will be. We estimate that a 21-layer filter made up of high refractive-index oxides and low refractive index SiO_2 may have an intrinsic error as high as 120%. It plausibly leads to a conclusion that PTDS is not applicable to measuring the absorption of a multilayer film due to large intrinsic error.

THE CALIBRATION ERROR

From Eq.(2), the calibration error is estimated as follows

$$dR/R = \left[(dA_c/A_c)^2 + (dV_c/V_c)^2 + (d\Delta V_c/\Delta V_c)^2 \right]^{1/2} \quad (13)$$

Ignoring scattering, we have $A_c=1-R_c-T_c$ where R_c and T_c are reflectance and transmittance of carbon-black thin film respectively, and hence,

$$dA_c/A_c = -(R_c/A_c) \cdot dR_c/R_c - (T_c/A_c) \cdot dT_c/T_c \quad (14)$$

Eq.(14) shows that large absorbance of carbon-black and small reflectance together with small transmittance generate small fractional error. The fractional error of carbon black is estimated to be 3% from data divergence in repeated measurements. Another candidate of calibration sample is metal but it does not serve so well as the carbon black does.

The intrinsic error of the calibration thin film can be calculated from Eqs.(4), (5) and (11) by substituting its parameters. For carbon-black

Table 1. The intrinsic errors of single-layer thin films at $\delta = \delta_{max}$

Mater.	MgO	GaAs	GaSb	Al ₂ O ₃	ZnO	TiO ₂	LiF	NaF	BaF ₂	MgF ₂	PbSe
Error(%)	36	32	27	12	10.3	7.8	8.8	6.5	6.5	1.9	2.6
Mater.	ZnS	CsBr	TlBr	Ba-Ti							
Error(%)	9.9	0.6	0.6	0.83							

and aluminum thin films, we have

$$\left. \frac{\Delta A_n}{A_n} \right|_{\delta=\delta_{\max}} = \begin{cases} 0.13 l & \text{for carbon black film} \\ 9.0 l & \text{for aluminum film.} \end{cases} \quad (15)$$

The intrinsic error of carbon black film is much smaller than that of a metal film of the same thickness. If $l=0.2 \mu\text{m}$, carbon black film has an intrinsic error of 2.6%. The error due to the incomplete identity of the calibration substrate and that of the optical thin film has also been considered. Practical measurements provide an estimate of 3.16%. The fractional error of instrument display is taken as 0.5%. All these estimates give an total fractional error $2.6\% + [(3\%)^2 + (3.16\%)^2 + (0.5\%)^2]^{1/2} = 6.96\%$.

THE MEASUREMENT ERROR

In addition to measurement errors caused by instrumental precision and reading, error in measurements is also generated by location of beams in different measurements due to inhomogeneity of film. The diversity of data in repeating measurements of a same sample gives an estimate of the location error of 1%. The former two errors are about 0.25% altogether. So the measurement errors sum to 1.1%.

TOTAL ERROR

In summary, the total error of PTDS measurement of the weak absorption of optical thin film is (following the maximum error method):

Total error = the intrinsic.+ the calibration.+ the measurement

- < 18.06% = 10% + 6.96% + 1.1% for most single-layer film;
- < 44.06% < 36% + 6.95% + 1.1% for some single-layer film with large heat conductivity such as MgO;
- > 100% for multilayer film due to large principled error.

CONCLUSION

Although the maximum method is adopted in estimating error, the total error of most single-layer optical films is still less than 18.06%. This means that PTDS measurement of weak absorption for them is highly precise since the measurable absorbance reaches the order of magnitude of 10^{-7} . However, for multilayer films, PTDS is in general not suitable to measure its absorbance because of large intrinsic error unless the total error can be controlled within 50% by homogenizing the pumping laser beam ($\delta=0$) and using materials with small heat conductivity or with less number of layers.

Calibration sample also affects the precision of PTDS measurements. Carbon-black thin film with the same substrate as optical films is recommended to serve as the calibration sample to minimize the intrinsic error.

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