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A posteriori error of the transmission interference method of thin film refractive index calculation

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Abstract. The method of *a posteriori* error calculation has been applied to the calculation of the refractive index and thickness of optical thin films from spectrophotometric transmission interference measurements. The refractive index and thickness of transparent or semitransparent thin film deposited on a transparent substrate can be calculated using both Edser–Butler and Swanepoel equations. A least-squares method and smoothing have been used to refine the Swanepoel's estimate and a correlation analysis has been applied to the differences between the two refractive index estimates. The refractive index covariance function is approximated by an exponential function and is then used in the statistical modelling process. The method has been applied to the calculation of the refractive index of a Sc_2O_3 thin film deposited on a quartz substrate. In practice the method is especially useful in view of its ability to detect the deterioration of data caused by instrumental drift.

1. Refractive index estimation

The refractive index and thickness of transparent or semitransparent thin films are usually determined from spectrophotometric measurements of their transmission. Using Swanepoel's method [1], the refractive index may be calculated as

$$\tilde{n}_i = \sqrt{N_i + \sqrt{N_i^2 - s_i^2}} \tag{1}$$

where $N_i = 2s_i(T_{Mi} - T_{mi})/(T_{Mi}T_{mi}) + (s_i^2 + 1)/2$, $s_i = 1/T_{si} + \sqrt{1/T_{si}^2 - 1}$, i is the number of the interference curve extremum, T_{Mi} and T_{mi} are the spectrophotometer measured maxima and minima transmissions of the thin films respectively and T_{si} is the transmission of the substrate without the film.

Using traditional approaches, the errors in $\tilde{n}_i$ may be determined in two ways: (1) from the errors in T_{Mi}, T_{mi} and T_{si} measurements; (2) repeating the whole experiment several times and calculating the dispersion of n_i by a well known formula. In our case both ways are practically very inconvenient because of instability of the spectrophotometer error, difficulty in controlling it and the relatively lengthy time of the measurement process. In this paper a method to determine the error of n_i is proposed which does not require the data of the errors of T_{Mi}, T_{mi}, T_{si} or repeated measurements. The estimate of n_i is obtained by a least-squares method from the interference equation

$$2n_i d = m_i \lambda_i \tag{2}$$

where m_i is the interference order (integer for maxima and half integer for minima), d is the film thickness and λ_i is the wavelength of number i extremum. The least-squares criterion is minimized, which is

$$I = \sum (\tilde{n}_i - \hat{n}_i)^2 \tag{3}$$

where $\tilde{n}_i$ is obtained by Swanepoel's estimate (equation (1)). $\hat{n}_i$ is the refractive index obtained from the interference equation (2), in which n_i and d are substituted with estimates $\hat{n}_i$ and $\hat{d}$:

$$\hat{n}_i = \frac{m_i \lambda_i}{2\hat{d}}. \tag{4}$$

The film thickness estimate $\hat{d}$ is produced by solving the equation $\partial I/\partial(1/\hat{d}) = 0$. Substituting $\hat{n}_i$ in equation (3) with equation (4) and solving the derivative ∂I gives

$$\hat{d} = \frac{\sum_i m_i \lambda_i / 2}{\sum_i \tilde{n}_i m_i \lambda_i}. \tag{5}$$

In the estimation process the interference order m_i is rounded off to integer or half integer.

In order to diminish the uncorrelated part of the error in this paper smoothing [2] is used:

$$\hat{n}_{si} = L[\hat{n}_i] \tag{6}$$

where L is the smoothing operator. The type and parameters of smoothing operator are not crucial for estimate quality, the only condition is to smooth 'slightly'.

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Table 1. Calculation of the refractive index of Sc_2O_3 thin film. m_i' is the interference order m_i before rounding off, 't' is the type of extremum (+ for maximum and − for minimum).

λ_i (nm)	t	T_{si}	T_{Mi}	T_{mi}	$\tilde{n}_i$	$\hat{n}_{si}$	α_i ($\times 10^6$ m^{-1})	m_i	m_i'	$\sigma\hat{n}_{si}$
340	+	0.924	0.868	0.740	1.962	1.916	116	7.500	7.684	0.016
364	−	0.925	0.879	0.764	1.907	1.906	70.8	7.000	6.975	0.016
386	+	0.925	0.890	0.787	1.860	1.886	37.1	6.500	6.416	0.015
414	−	0.932	0.900	0.790	1.848	1.867	48.6	6.000	5.945	0.015
448	+	0.933	0.907	0.794	1.849	1.852	37.1	5.500	5.495	0.015
492	−	0.933	0.918	0.787	1.895	1.848	22.6	5.000	5.128	0.015
546	+	0.938	0.912	0.783	1.874	1.846	58.1	4.500	4.570	0.015
615	−	0.939	0.910	0.792	1.838	1.842	43.7	4.000	3.980	0.015
695	+	0.939	0.905	0.813	1.762	1.828	8.99	3.500	3.376	0.016

The least-squares estimate (5) may be compared with that proposed in [3], which is $\bar{d} = \sum \bar{d}_i/N$, where $\bar{d}_i = m_i\lambda_i/2\tilde{n}_i$ and N is the total number of extremes. The estimate (5) has a more even distribution of weight, but it is not significant and we think that the statistical errors of those estimates are close. The values of the mean squares errors $\sigma\bar{d}_i$ in [3] cannot be used to obtain the resulting error $\sigma\bar{d}$ because of the substantial autocorrelatedness of $\tilde{n}_i$ and therefore also of $\bar{d}_i$.

2. Calculation of *a posteriori* error

In order to obtain the refractive index and thickness errors it was assumed that the stochastic process $Y_i = \tilde{n}_i - \hat{n}_i$ is stationary, i.e. independent of its dispersion on i. In fact, this is not the case, but sequence Y_i is quite short ($N < 20$, where N is total number of extremes) and the fact that it is not stationary is completely masked by its random behaviour. The values of $\tilde{n}_i$ and $\hat{n}_i$ are uncorrelated; therefore the dispersion of Y_i, which due to supposition is constant, is

$$DY = D\tilde{n} + D\hat{n}. \tag{7}$$

From measurements it can be estimated as

$$\hat{D}Y = 1/(N-1)\sum_i Y_i. \tag{8}$$

Measurements of λ_i are independent, therefore the error in $\hat{n}_i$ is not autocorrelated and its dispersion can be estimated as [4]

$$\hat{D}\hat{n} = \frac{2}{3(N-2)}\sum_{i=2}^{N-1}\left(\hat{n}_i - \frac{\hat{n}_{i-1}+\hat{n}_{i+1}}{2}\right)^2. \tag{9}$$

From equations (7)–(9) the dispersion of Swanepoel's estimate is

$$\hat{D}\tilde{n} = \hat{D}Y - \hat{D}\hat{n}. \tag{10}$$

The covariance function of $\hat{n}_i$ differs from zero only when $i = 0$, therefore the covariance function of $\tilde{n}_i$ may be estimated as

$$R_j = \frac{1}{N-j}\sum_{i=1}^{N-j} Y_i Y_{i+j} \tag{11}$$

and $R_0 = \hat{D}Y - \hat{D}\hat{n}$. The covariance function R_j in this paper is approximated by

$$\tilde{R}_j = \hat{D}\tilde{n}\exp(-|j|/\rho) \tag{12}$$

where $\rho = \sum r_j$, the sum over j while $r_j = R_j/\hat{D}\tilde{n} > 0$.

The dispersions of the estimates $\hat{n}_{si}$ and $\hat{d}$ are calculated by means of statistical modelling for formulae (5) and (6) in which input sequences $\tilde{n}_i$ and λ_i are substituted by pseudostochastic sequences

$$n_i^* = \hat{n}_{si} + z_i \qquad \lambda_i^* = \hat{\lambda}_{si} + D\lambda_i \cdot X_i \tag{13}$$

where z_i is an autocorrelated stationary sequence with a covariance function (12), which has been calculated using an iterative process [5] $z_i = az_{i-1} + bX_i$, $z_0 = \sqrt{Dz}\cdot X_0$, where $a = \exp(-1/\rho)$, $b = \sqrt{Dz(1-a^2)}$, $Dz = \hat{D}\tilde{n}$. The uncorrelated Gaussian stochastic process X_i with zero mean and standard dispersion is produced by a pseudostochastic numbers generator. Refined values of the wavelengths are $\hat{\lambda}_{si} = 2\hat{d}\cdot\hat{n}_{si}/m_i$. The error of λ_i is derived from equation (2) by taking into consideration that participation of the error of $\hat{d}$ is not significant comparing with that of $\hat{n}_i$, therefore

$$D\lambda_i = \frac{4\hat{d}^2}{m_i^2}\hat{D}\hat{n}.$$

In summary the calculation algorithm for $\hat{n}_{si}$, $\hat{d}$ and its errors consists of the following steps.

(1) Calculation of Swanepoel's estimate $\tilde{n}_i$ by equation (1).

(2) Calculation of $\hat{d}$ and $\hat{n}_{si}$ by (5) and (6).

(3) Calculation of Swanepoel's estimate dispersion $\hat{D}\tilde{n}$ by (10).

(4) Calculation of R_j by (11) and exponent index ρ.

(5) Statistical modelling of formulae (5) and (6), which gives the dispersion of estimates $\hat{n}_{si}$ and $\hat{d}$.

3. Experimental results

This algorithm was used for the investigation of optical properties of rare earth oxide thin films. By means of reactive synthesis (electron beam evaporation of metallic scandium in oxygen environment) the Sc_2O_3 thin film was deposited onto a polished quartz substrate. Before deposition the transmission of the substrate without film T_{si} was measured using a spectrophotometer (SPECORD UV VIS). After the deposition the interference curve of the thin film was obtained using the same spectrophotometer and T_{Mi}, T_{mi}, λ_i were obtained from this curve. The

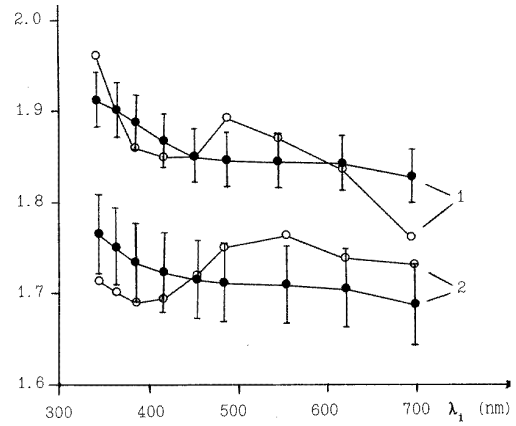

Figure 1. Dependence $n(\lambda)$ for Sc_2O_3 film: ○, $\tilde{n}_i$ calculated with Swanepoel's method; ●, $\hat{n}_{si}$ calculated with equation (6) with its confidence intervals, calculated as $\pm 2\sigma\hat{n}_{si}$. Curves 1, before annealing; 2, after annealing.

results of processing these data with the algorithm are given in table 1. The absorption coefficient of the film substance was calculated as $\alpha_i = -\ln x_i/\hat{d}$, where absorbance x_i according to [1] is $x_i = [E_{Mi} - \sqrt{E_{mi}^2 - (\hat{n}_{si}-1)^3(\hat{n}_{si}^2 - s_i^4)}]/(\hat{n}_{si}-1)^3(\hat{n}_{si} - s_i^2)$ where, for maxima, $E_{Mi} = 8\hat{n}_{si}^2 s_i/T_{Mi} + (\hat{n}_{si}^2 - 1)(\hat{n}_{si}^2 - s_i^2)$. For minima E_{Mi} must be substituted by $E_{mi} = 8\hat{n}_{si}^2 s_i/T_{mi} - (\hat{n}_{si}^2 - 1)(\hat{n}_{si}^2 - s_i)$. The values of α_i in table 1 are unstable, which shows the error in α_i is too great in comparison with the values of α_i.

After these measurements the sample was annealed in a muffle chamber (673 K for 2 h) and the interference curve was again obtained using the same spectrophotometer. Figure 1 shows the dependence $n(\lambda)$ before and after annealing.

After annealing the refractive index substantially decreased. This may be explained by assuming that the deposited layer was not stoichiometric and had a surplus of metal ions which increase the refractive index. The annealing process oxidized the coating and the refractive index decreased. In both cases the refractive index is less than that of bulk scandium oxide, which is $n = 1.990$ for yellow sodium line $\lambda = 589.3$ nm. This may be explained as being due to the presence of defects in the coating lattice.

Table 2 shows some calculation results, $\sigma(\cdot) = \sqrt{D(\cdot)}$.

The increase in film thickness after annealing is due to the incorporation of extra oxygen atoms with a consequent rearrangement of the lattice structure. The thickness increase is substantially greater than the error $\sigma\hat{d}$.

Table 2. Calculation results.

	$\hat{d}$ (nm)	$\sigma\hat{d}$ (nm)	$\sigma\tilde{n}$	$\sigma\hat{n}$
Before annealing	666	5	0.034	0.006
After annealing	725	11	0.041	0.007

Comparison of $\sigma\tilde{n} = 0.034$ (table 2) with $\sigma\hat{n}_{si}$ (table 1) shows that the described method diminishes the error obtained by Swanepoel's method [1] by approximation one half. Figure 1 shows that the least-squares approximation and smoothing have made the dependence $n(\lambda)$ more smooth and decrease monotonically, which is in accordance with light dispersion theory. The uncorrelated part $\sigma\hat{n}$ is approximately 1/3 of $\sigma\hat{n}_{si}$, which is substantial—it proves the necessity of auxiliary smoothing (equation (6)).

The method has also been used to investigate the effect of growth conditions on the optical properties of Y_2O_3 thin films [6].

A further development of the work is to apply this approach to Swanepoel's second method [7], which deals with thin films with inhomogeneous thickness distributions.

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