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DETERMINATION OF OPTICAL PARAMETERS AND THICKNESS OF THIN FILMS DEPOSITED ON ABSORBING SUBSTRATES USING THEIR REFLECTION SPECTRA*

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The wavelength – dependent refractive index, extinction coefficient as well as the thickness of the film can be found by various spectrophotometric techniques. When the film is deposited on transparent substrate, the so–called envelope method used for transparent films with interference effects in transmittance and reflectance spectra is available. However, when the film is deposited on thick absorbing substrate, only spectral reflectance measurements are possible. The optimised envelope method is suitable to solve for optical parameters of thin films on absorbing substrates simultaneously. The algorithm assuming a thin isotropic film with parallel interfaces is described here. Moreover, in this study the spectrophotometric iso reflectance contours method is shown to be a powerful tool for determining the film thickness. Both methods are presented using a hypothetical film. The error analysis of the simulated reflectance spectrum shows the advantages and limitations of the methods. It is reported that the main source of errors in determining the optical constants and the thickness is associated with reflectance measurements. The methods described here are applied for determining the optical parameters of ZnO and Y_2O_3 thin films deposited by rf diode sputtering on Si substrates.

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1 Introduction

Thin films have received increasing attention due to their wide range of optical and opto–electronic applications. Optical characterisation of thin films gives information about other physical properties, e.g. band gap energy and band structure, optically active defects etc. and therefore may be of permanent interest for several different applications. Considerable differences between optical constants of bulk material and thin films or those of films prepared under varying growth characteristics are often reported. Therefore optical constants determination of each individual film by a non–destructive method is highly recommended. Optical measurements are mostly

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carried out by spectrophotometry or spectroscopic ellipsometry. The difference between various optical techniques is in the choice of at least two measurements of reflected or transmitted light and in the way of the inversion of reflection or transmission data to obtain the optical constants values [1–10].

In this study, the optical constants and the thickness of the films were determined by two optical techniques using interference reflection spectroscopy.

2 Interference reflection spectrophotometry

The spectral refractive index, extinction coefficient as well as the thickness of the film can be found by a transmittance $T(\lambda)$ or a reflectance $R(\lambda)$ spectrum of the film deposited on transparent substrate. When the film is deposited on thick absorbing substrate, only spectral reflectance measurement is possible.

Optical reflection of an ideal parallel–sided thin film on a thick substrate illuminated at nearly normal incidence with monochromatic radiation can be described by simple theory of classical physical optics. A thin isotropic film with the average thickness d is characterised by the complex refractive index $n_1 = (n_1 - ik_1)$ and the substrate (with the thickness $\gg d$) by the complex refractive index $n_2 = (n_2 - ik_2)$, where $n_1(n_2)$ is the real part of the complex refractive index, the imaginary part $k_1(k_2)$ is the extinction coefficient. The optical reflectance of a parallel–sided thin isotropic homogeneous film on a thick partly absorbing substrate, both immersed in air, is given by

$$R = \frac{A + Bx + Cx^2}{D + Ex + Fx^2} \qquad (1)$$

where $x = \exp(-\alpha d)$ is the absorbance, $\alpha = (4\pi k_1)/\lambda$ is the absorption coefficient, $\phi = (4\pi n_1 d)/\lambda$,

$$\begin{aligned}
A &= [(1-n_1)^2 + k_1^2][(n_1+n_2)^2 + (k_1+k_2)^2],\\
C &= [(1+n_1)^2 + k_1^2][(n_1-n_2)^2 + (k_1-k_2)^2],\\
D &= [(1+n_1)^2 + k_1^2][(n_1+n_2)^2 + (k_1+k_2)^2],\\
F &= [(1-n_1)^2 + k_1^2][(n_1-n_2)^2 + (k_1-k_2)^2],\\
B &= 2[A'\cos\phi + B'\sin\phi], \qquad E = 2[C'\cos\phi + D'\sin\phi],\\
A' &= (1-n_1^2-k_1^2)(n_1^2-n_2^2+k_1^2-k_2^2) + 4k_1(n_1k_2-n_2k_1),\\
B' &= 2(1-n_1^2-k_1^2)(n_1k_2-n_2k_1) - 2k_1(n_1^2-n_2^2+k_1^2-k_2^2),\\
C' &= (1-n_1^2-k_1^2)(n_1^2-n_2^2+k_1^2-k_2^2) - 4k_1(n_1k_2-n_2k_1),\\
D' &= 2(1-n_1^2-k_1^2)(n_1k_2-n_2k_1) + 2k_1(n_1^2-n_2^2+k_1^2-k_2^2).
\end{aligned} \qquad (2)$$

Optical constants can be deduced from a non–linear equation

$$R(\lambda_i, n_1, k_1, d) - R_{exp} = 0. \qquad (3)$$

Since the equation is not reversible, a fitting procedure is necessary to calculate n_1, k_1, d and get the best fit between the measured reflectance R_{exp} and the calculated value R. The calculated reflectance $R(\lambda_i, n_1, k_1, d)$ is according to Eqs. (1), (2) the function of three parameters

n_1, k_1, d and can be fitted to the measured reflectance R_{exp} by several approaches – by numerical solution of Eq. (3), by minimising the sum of the squares of the deviations at all wavelengths $\sum_i [R_{exp}(\lambda) - R(\lambda_i, n_1, k_1, d)]^2$ and looking for global minimum or local minima for each parameter.

3 Envelope method

In the interference – especially in the transmittance – spectrophotometry, the envelope method is often used [1–6]. Obviously, from a single reflectance measurement only one independent parameter can be determined. When the film is slightly absorbing, interference effects coming from multiple coherent reflections at the interfaces are present in the reflectance spectrum and the above parameters can be determined from the envelopes R_{max} and R_{min} along the interference maxima and minima. The widely used version of envelope method has been developed by Swanepoel [1] for transmittance measurement. Versions based on the reflectance alone are infrequent [7,10,11], the extraction of the optical constants is more involved and very different.

The reflectance R can be expressed for the envelopes of the interference fringes using the conditions for the interference maxima $2n_1 d = m\lambda$ and the interference minima $2n_1 d = (2m + 1)\lambda/2$, $|m| = 0, 1, 2...$ Thus, the envelopes of the interference maxima R_{max} and interference minima R_{min} are given by Eq. (1) with parameters A, C, D, F according to Eq. (2), but with following parameters (for $n_1 < n_2$) for R_{max}

$$\begin{aligned} B &= 2[(1 - n_1^2 - k_1^2)(n_1^2 - n_2^2 + k_1^2 - k_2^2) + 4k_1(n_1 k_2 - n_2 k_1)], \\ E &= 2[(1 - n_1^2 - k_1^2)(n_1^2 - n_2^2 + k_1^2 - k_2^2) - 4k_1(n_1 k_2 - n_2 k_1)] \end{aligned}$$

and for R_{min}

$$\begin{aligned} B &= 2[(1 - n_1^2 - k_1^2)(n_1^2 - n_2^2 + k_1^2 - k_2^2) + 4k_1(n_1 k_2 - n_2 k_1)], \\ E &= -2[(1 - n_1^2 - k_1^2)(n_1^2 - n_2^2 + k_1^2 - k_2^2) - 4k_1(n_1 k_2 - n_2 k_1)]. \end{aligned} \quad (4)$$

Equations for R_{max}, R_{min} are non–linear equations of n_1, k_1. Expressing x from R_{max}, R_{min} and equating them, a polynomial for independent parameters n_1, k_1 is obtained at each wavelength. The optical parameters n_1, k_1 are determined numerically in several steps.

In the reflectance spectrum with the interference fringes the assumption $n_1^2 \gg k_1^2$ is valid. Assuming this in the polynomial obtained from R_{max}, R_{min}, we numerically solve for n_1 and the initial value of k_1. Assuming R_{max}, R_{min} to be continuous functions of the wavelength, n_1, k_1 as functions of λ can be obtained. The initial value of k_1 is used in the recalculation of n_1, k_1 according to the above procedure without the assumption $n_1^2 \gg k_1^2$. The procedure of successive iterations should be repeated until the satisfactory accuracy in n_1, k_1 is obtained.

Knowing n_1 as the function of λ, we calculate the thickness d according to the standard equation for two adjacent interference fringes at wavelengths λ_m, λ_n: $d = \frac{\lambda_m \lambda n}{2(\lambda_m n_n - \lambda_n n_m)}$ (n_m, n_n are refractive indices corresponding to these wavelengths). The average value of d is taken to find the order number of interference fringes. With order numbers deduced, one recalculate the film thickness with the same n_1 as before. The improved thickness is used to perform the procedure again and to improve n_1 and k_1. With improved values of k_1 and d, the absorption coefficient α can be calculated.

The method suffers from multiple solutions n_1, k_1 of the polynomial. However, the identification of the correct solution without any other independent measurement is possible [2,10]. The general procedure how to find the correct solution is to adjust the thickness and the optical parameters to acceptable results of dispersion dependence and to use constraints restricting the number of degrees of freedom but requiring some prior physically meaningful knowledge of the material.

4 Iso reflectance contours method

The novel method of determining the thickness of the film presented here can be considered as R, R_{max}, R_{min} inversion method and is limited to the wavelength interval where the interference effects in reflectance spectra occur. Optical constants are solutions of the set of equations

$$R(n_1, k_1, d, \lambda) - R_{exp}(\lambda) = 0, \tag{5}$$

$$R_{max}(n_1, k_1, d, \lambda) - R_{expmax}(\lambda) = 0, \tag{6}$$

$$R_{min}(n_1, k_1, d, \lambda) - R_{expmin}(\lambda) = 0 \tag{7}$$

where R_{exp}, R_{expmax}, R_{expmin} are experimental values at the wavelength λ, R, R_{max}, R_{min} calculated values according to Eqs. (1)-(4). If we plot the iso contours of R, R_{max}, R_{min} at one wavelength in the n_1, k_1 – plane and if d used in calculations is correct, an intersection of all three curves occurs. Consequently d and the functions $n_1(\lambda)$ and $k_1(\lambda)$ are obtained. It is expected the method using all spectral points gives better accuracy than the one using only the interference extrema.

For solving Eqs. (5)-(7) a pointwise iteration method in the parameter space (n_1, k_1, d) was used. It must be provided the iteration method to converge to the right point. In our calculations, gradient approaching near the intersection was applied. The condition for the convergence of 0.0001 was set, well below the reasonably required accuracy of n_1, k_1. Iso contours are sensitive to the value of d especially when the three curves intersect at large angles.

5 Simulations

The validity of both reflectance methods was tested using hypothetical reflectance characteristics. The Forouhi and Bloomer dispersion equations have been often reported as well–established for photon energy dependence of n_1 and k_1 of many amorphous dielectrics and semiconductors [12]. If E denotes the photon energy, the equations are of the following form:

$$\begin{aligned} n(E) &= n(\infty) + \frac{B_0 E + C_0}{E^2 - BE + C}, \qquad k(E) = \frac{A\big(E - E_g\big)^2}{E^2 - BE + C}, \\ B_0 &= \frac{A}{Q}\left(-\frac{B^2}{2} + E_g B - E_g^2 + C\right), \qquad C_0 = \frac{A}{Q}\left(\big(E_g^2 + C\big)\frac{B}{2} - 2E_g C\right), \\ Q &= \frac{1}{2}\sqrt{4C - B^2}. \end{aligned} \tag{8}$$

The following parameters of the film on Si substrate were assumed $A = 0.03, B = 6.48, C = 10.6, E_g = 2.65, n(\infty) = 1.85$ and the thickness $d = 1200$ nm. The optical parameters and

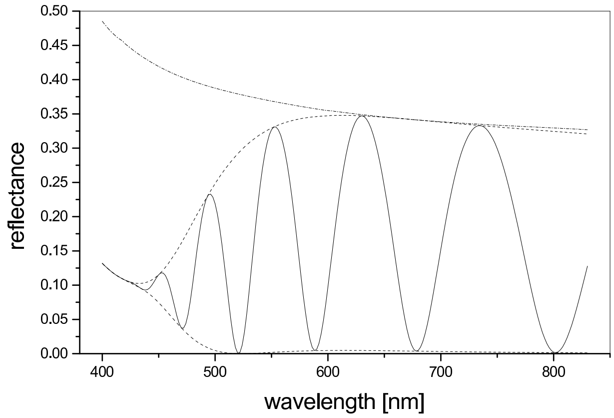

Fig. 1. Reflectance of the hypothetical film (solid curve), of the envelopes (dashed curves), of the Si substrate (dashed–dotted curve).

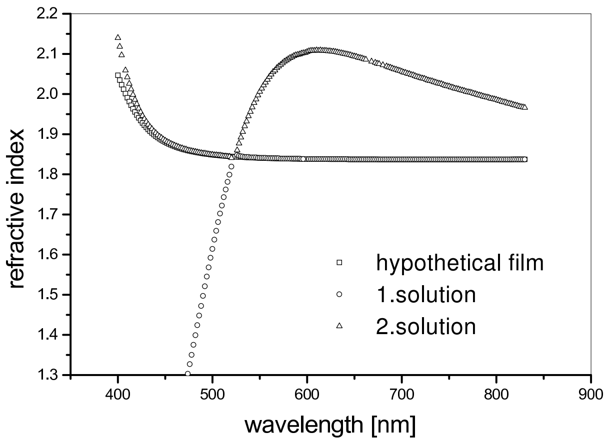

Fig. 2. Theoretical values and two solutions for n_1 of the hypothetical film.

reflectance of hypothetical film are in Fig. 1 and 2. The optical parameters n_2, k_2 of the Si substrate were taken from [13].

6 Hypothetical film and the envelope method

To get smooth envelopes R_{expmax}, R_{expmin}, the non–linear least squares interpolation between turning points of the reflectance spectrum (Fig. 1) was made by the Levenberg – Marquardt algorithm. The envelope method applied to the R_{expmax}, R_{expmin} of the hypothetical film gave two mathematical solutions of n_1 and k_1 (Figs. 2, 3). Hypothetical values of n_1, k_1 given by the Forouhi and Bloomer model were reconstructed from these two solutions. Note, that the only differences between the hypothetical and retrieved values were observed for $\lambda < 430$ nm, where

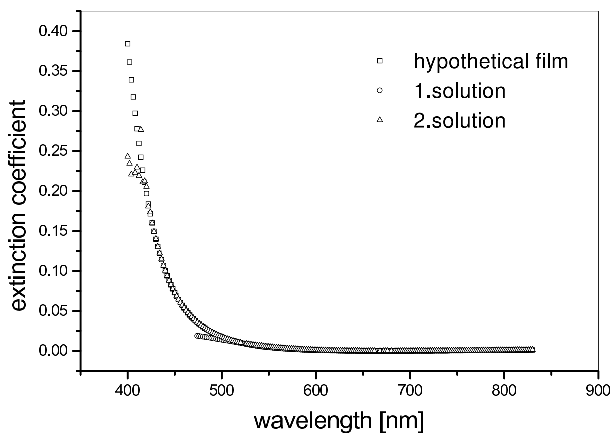

Fig. 3. Hypothetical film – theoretical values and two solutions for k_1.

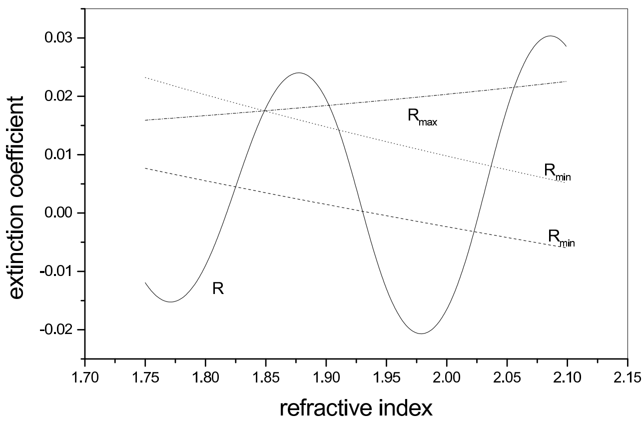

Fig. 4. Iso reflectance contours for the hypothetical film at the wavelength 500 nm.

the envelopes apparently converge toward each other owing to increasing absorption of light in the film. The original film thickness $d = 1200$ nm was also retrieved. The close reconstruction of the originally assumed parameters reveals the power of the method.

7 Hypothetical film and the iso contours method

Fig. 4 illustrates the iso reflectance contours for the hypothetical film. The curves R, R_{max}, R_{min} calculated for $\lambda = 500$ nm with the step of $n_1 = 0.001$ and the step of $k_2 = 0.00002$ intersect in the n_1, k_1 – plane using the correct thickness $d = 1200$ nm. The intersection in n_1, k_1 – plane can be localised with satisfactory accuracy.

Iso contours are found to be very sensitive to the film thickness (Fig. 5). Therefore, if there

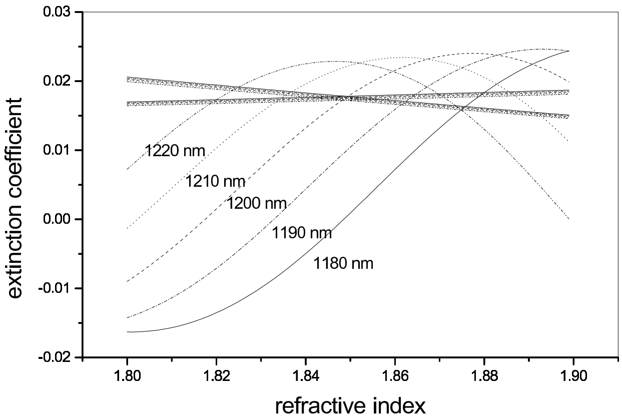

Fig. 5. Iso reflectance contours for the changing thickness, the intersection only for $d = 1200$ nm.

is the thickness variation effect throughout the sample, the method could be a tool to investigate the thickness inhomogeneities if the spectrophotometer resolution is big enough.

8 Error analysis

R, R_{max}, R_{min} according to Eqs. (5)-(7) depend on experimental values R_{expmax}, R_{expmin}, R_{exp} and on the substrate parameters n_2, k_2. The errors of R_{expmax}, R_{expmin}, R_{exp}, n_2, k_2 propagate to the intersection position and therefore to errors of n_1, k_1, d. The numerical analysis shows that especially accurate knowledge of values R_{expmax}, R_{expmin}, R_{exp} is of vital importance and great care must be given to constructing smooth envelopes $R_{expmax}(\lambda)$, $R_{expmin}(\lambda)$.

Simulation results are in Figs. 6-8 for $\lambda = 550$ nm. The original hypothetical values are $n_1 = 1.849$, $k_1 = 0.0175$. The propagation of the error $\Delta R_{expmax} = \pm(0.01, 0.02)$ is in Fig. 6. The shift of the $R_{expmax} = 0.25$ by ± 0.02 results in the shift of the intersection. The values of n_1 are then in the interval $\sim (1.81 - 1.88)$, $k_1 \sim (0.012 - 0.02)$ and $d \sim (1165 - 1240)$ nm. The similar numerical analysis in Fig. 7 for $R_{expmin} = 0.0046$ with $\Delta R_{expmin} = \pm 0.002$ results in $n_1 \sim (1.812 - 1.875)$, $k_1 \sim (0.013 - 0.018)$ and $d \sim (1190 - 1220)$ nm. As the construction of smooth envelope R_{expmin} is more involved than R_{expmax}, the influence of the R_{expmin} accuracy becomes apparent. The analysis for two overestimates of R_{expmin} shows d changing from 1030 nm ($R_{expmin} = 0.01$) to 1280 nm ($R_{expmin} = 0$), the n_1 interval is much wider $(1.73 - 1.92)$, the change of k_1 is comparable to the previous case. The influence of the change of $R_{exp} = 0.22$ by ± 0.02 (Fig. 8) on n_1, k_1 is negligible, d changes only $\sim (1196 - 1207)$ nm. The influence of the change of the refractive index of the substrate n_2 on d and n_1 is not significant. The change of k_2 results in negligible errors of d, k_1. The n_1 error was found to be < 0.01.

The error analysis at the turning point of the reflectance (maximum 552 nm) shows the change of $n_1 \sim (1.79 - 1.89)$ and $d \sim (1170 - 1230)$ nm while R_{expmax}, R_{exp} changing by ± 0.02. The accuracy of iso method at the minimum points was found to be worse. Therefore, the iso method usage should be recommended at wavelengths far out of the turning points.

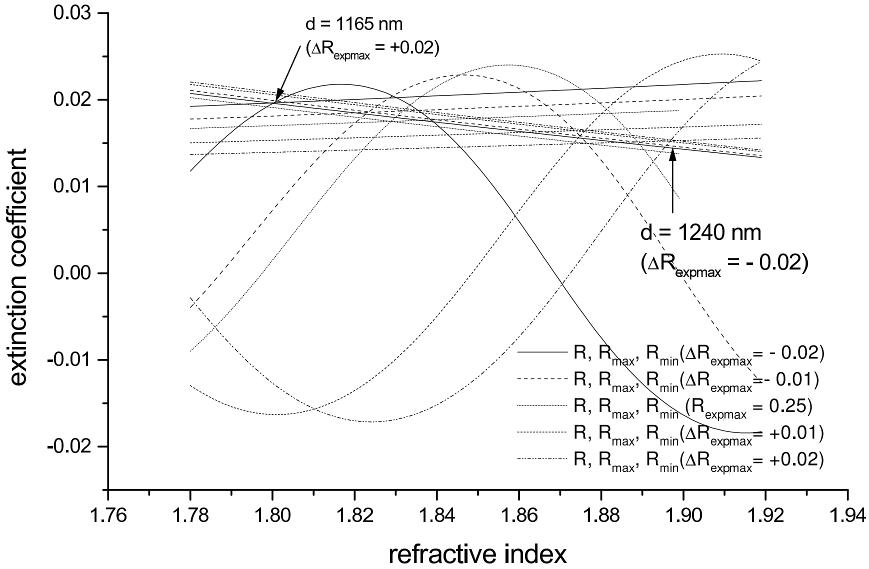

Fig. 6. Influence of R_{expmax} on iso contours.

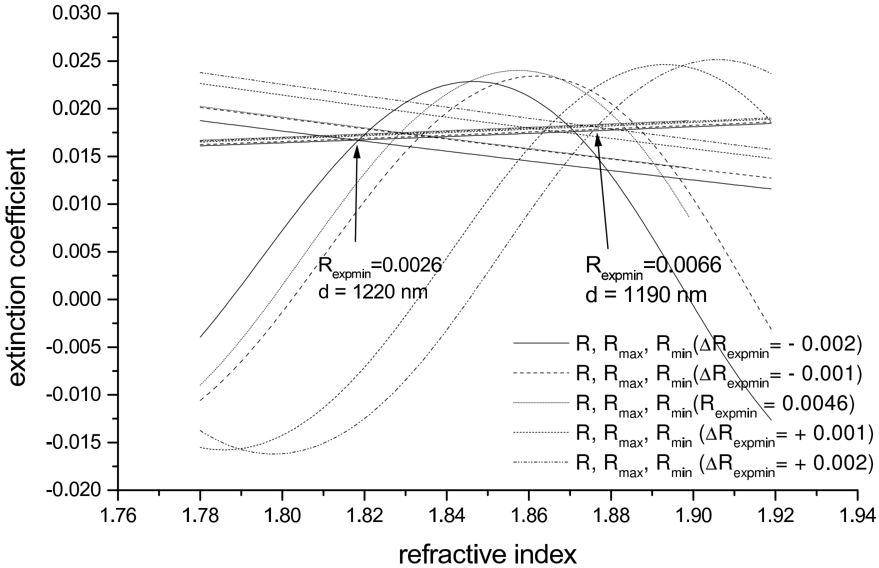

Fig. 7. The influence of R_{expmin} on iso contours.

Further remarks on the accuracy are concerned with the envelope method. Obviously there are no difficulties with establishing interference fringes with common digital spectrophotometers,

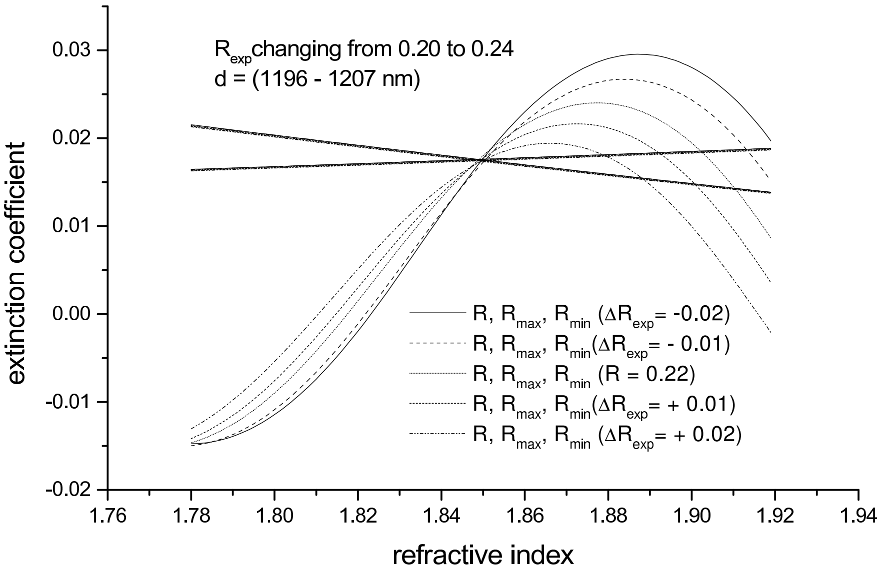

Fig 8. The influence of R_{exp} on iso contours.

a good algorithm with a local polynomial smoothing is necessary for constructing the envelopes. The main source of error comes from reflectance measurements, especially from R_{expmin}. The accuracy of $\Delta n_1 \sim 0.02$ at $R_{expmax} = 0.01$ and $\Delta n_1 \sim 0.02$ at $R_{expmin} = 0.005$ was obtained. Errors introduced to n_1, k_1 increase when approaching to the absorption edge and when $n_1 \sim n_2$ (interference effects vanish from the reflectance spectrum then). The error of the averaged d calculated for various wavelength (by the iso method) and for many adjacent interference extrema (by the envelope method) is believed to be less than the value in simulated error analysis at one wavelength. Additional errors are due to the departures from ideal experimental conditions: continuous thickness variations over the sample, refractive index fluctuations, the roughness of the thin film surface, the non–zero bandwidth of the spectrophotometer, especially when it varies with the wavelength.

9 Experimental

The thin film samples under study ZnO and Y_2O_3 were deposited on the optically polished Si by rf diode sputtering under deposition parameters described elsewhere [14]. The thickness of ZnO thin film estimated from deposition conditions was 1000 nm, the value determined by a stylus–based surface profiler Talystep was 700 nm. The corresponding values for Y_2O_3 film were 400 nm/283 nm.

Reflectance measurements were carried out by a double–beam Carl Zeiss Jena spectrophotometer Specord M40 with the slit of 2.5 nm at room temperature. An accessory for absolute reflectance measurement at nearly normal incidence was used with a freshly evaporated aluminium sample in the reference beam and special care was taken to provide the reproducibility

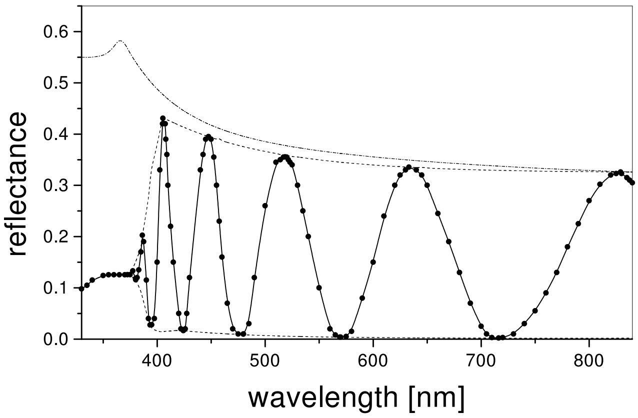

Fig. 9. ZnO/Si reflectance (solid line), the envelopes (dashed), bare Si reflectance (dashed–dotted line).

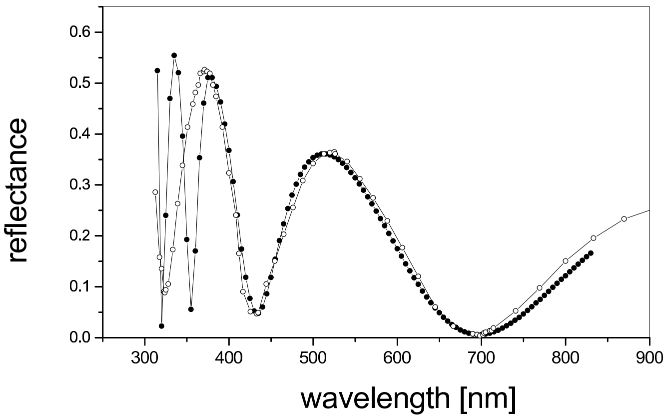

Fig. 10. Y_2O_3/Si reflectance, open points – experimental values, solid points – retrieved reflectance.

of measurements. The absolute errors of the reflectance measurements were ~ 0.01. Interference effects are apparent (Figs. 9, 10). The values of n_2, k_2 were taken from [13] and confirmed by the Kramers–Kronig dispersion analysis of Si substrate reflectance spectrum. No significant differences were found between the reflection spectra from different areas of the samples. As the probed area was ~ 0.2 cm^2, at least down to this scale the films can be considered homogeneous.

10 Results

The thickness was determined by the iso method applied to several spectral points of both reflectance spectra and the final averaged values $d(\text{ZnO}) = 700$ nm $\pm 4\%$, $d(\text{Y}_2\text{O}_3) = 305$ nm $\pm 6\%$ are almost in complete agreement with the stylus–determined values. Therefore, there is no

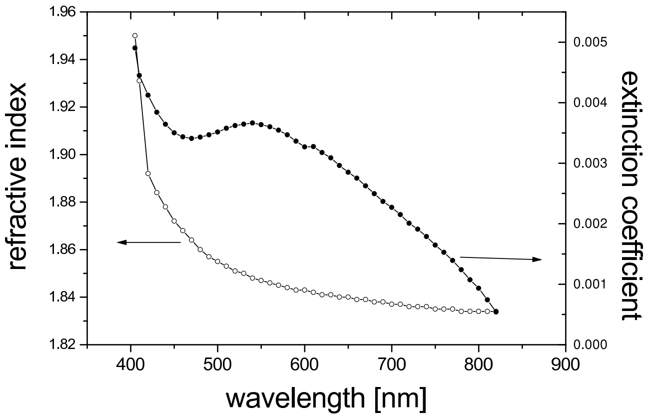

Fig. 11. Optical constants of ZnO thin film.

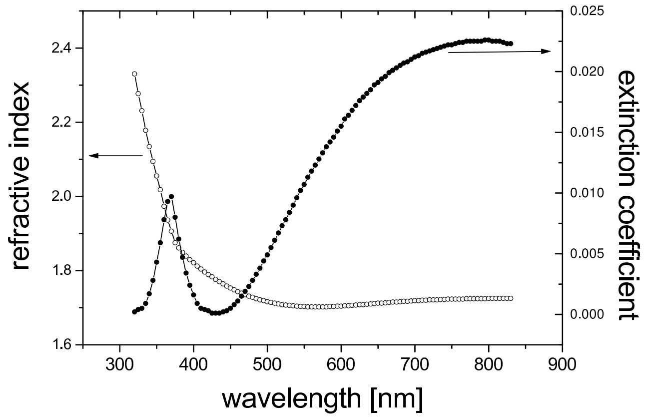

Fig. 12. Optical constants of Y_2O_3 thin film.

need to determine the accurate film thickness by an independent measurement, although at least estimated values benefit to rejecting physically less meaningful solutions. The optical constants of samples under study retrieved by the envelope method are in Figs. 11 and 12. They are smaller than values reported for bulk material.

The comparison of experimental and retrieved reflectance for Y_2O_3 in Fig. 10. The satisfactory fit is observed for $\lambda > 370$ nm. Similar results are observed for ZnO for $\lambda > 400$ nm. The possible errors can be associated to the non–parallelism of the interfaces, inhomogeneity of the film and surface roughness. The most probable explanation for the poorer fit at smaller wavelengths is the finite bandwidth $(\Delta\lambda \neq 0)$ of the spectrophotometer. It was reported that the consequence of the bandwidth effect is the shrinkage of the interference extremes [15]. The method using only envelopes is apparently less susceptible to the differences between measured and calculated ideal reflectance introduced by finite bandwidth. We aim to explore the effects of departures from ideal film structure in future.

11 Conclusion

The investigation of the retrieval of the wavelength-dependent refractive index, extinction coefficient and the thickness of thin films from the reflectance spectra only has been demonstrated. The methods presented here can be applied to reflectance data of any thin film in which interference effects occur. As the procedure relies on the reflectance measurement alone, its outstanding advantage is the simplicity of obtaining the experimental data.

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