

## ON THE DETERMINATION OF THE OPTICAL CONSTANTS OF VERY THIN ( $\lambda/50$ ) FILMS

P. Gushterova<sup>\*</sup>, P. Sharlandjiev, B. Schmidt<sup>a</sup>, M. Pham<sup>a</sup>

Central Laboratory for Optical Storage and Processing of Information, Bulgarian Academy of Sciences, "Acad. G. Bontchev" Str., Bl. 101, Sofia 1113, Bulgaria

<sup>a</sup>Institute of Ion Beam Physics and Materials Research, Forschungszentrum Rossendorf, POB 51 01 19, 01314 Dresden, Germany

The improvement of a recently developed spectrophotometric method for the determination of the complex refractive index ( $\tilde{n}$ ) and physical thickness ( $d$ ) of very thin films ( $d \cong \lambda/50$ ,  $\lambda$  is the wavelength in the visible and near infrared) is presented. The thin film transmittance ( $T_f$ ), front side reflectance ( $R_f$ ) and back side reflectance ( $R'_f$ ) are used for the estimation of ( $\tilde{n}$ ,  $d$ ). Utilizing the nanothickness of the films, we derive analytical expressions for  $R_f$ ,  $R'_f$  and  $T_f$ , by development of the Abelès characteristic matrix elements up to the 4th order in  $\tilde{n}d/\lambda$ . An optimization procedure is used to estimate ( $\tilde{n}$ ,  $d$ ). Thus, the problem related to multiple or lack of solutions is overcome. The method is applied to Au films, deposited on transparent glass substrates. For comparison of the resulting ( $\tilde{n}$ ,  $d$ ), Veritable Angle Spectroscopic Ellipsometry is used as an independent technique.

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### 1. Introduction

For the needs of nanotechnology, new methods for the characterization of films with thicknesses ( $d$ ) between a few nanometers and a few tens of nanometers have been developed. Several recently developed spectrophotometric [1,2] and ellipsometric [3] methods for the determination of the optical constants ( $n$  – refractive index and  $k$  – extinction coefficient) and thicknesses of nanolayers can be found in the literature. However, they have their limitations, i.e., some [1,2] are applicable only for thin films with  $d > 30$  nm. Ellipsometry is a well-established, straightforward technique for the estimation of ( $n$ ,  $k$ ,  $d$ ) of thin films.

In a recent publication [4], we reported a method for the determination of ( $n$ ,  $k$ ,  $d$ ) of very thin films ( $d < \lambda/50$ , where  $\lambda$  is the wavelength). In this method, after limited development of the trigonometric functions of the thin film characteristic matrix elements up to the third order in terms of  $\tilde{n}d/\lambda$ , ( $\tilde{n} = n - ik$  is the complex refractive index of the film), approximate expressions for the film front side reflectance ( $R_f$ ), back side reflectance ( $R'_f$ ) and transmittance ( $T_f$ ) were obtained. By solving the set of the equations  $(1+R_f)/T_f$ ,  $(1-R_f)/T_f$  and  $(1-R'_f)/T_f$ , simple analytical expressions for ( $n$ ,  $k$ ,  $d$ ) as functions of  $R_f$ ,  $R'_f$  and  $T_f$  were derived. The approach is very fast and effective for the evaluation of ( $n$ ,  $k$ ,  $d$ ) of very thin films from spectrophotometric measurements with normal incidence of light in the visible (VIS) and near infrared (NIR) wavelength regions.

In this paper, we report an improvement on the method [4]: the film characteristic matrix elements are developed to the fourth order in terms of  $\tilde{n}d/\lambda$ . The system of equations  $(1+R_f)/T_f$ ,  $(1-R_f)/T_f$  and  $(1-R'_f)/T_f$  is solved numerically. This improvement allows us to increase the accuracy of

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<sup>\*</sup> Corresponding author: pgushterova@dir.bg

the estimated  $(n, k, d)$  values, and also to use the method for the determination of  $(n, k, d)$  of metal films (low  $n$ , very high  $k$ ). We apply the method to estimate  $(n, k, d)$  of evaporated Au films with  $d$  between 10 and 30 nm. For comparison of the estimated  $(n, k, d)$  values, Variable Angle Spectroscopic Ellipsometry (VASE) is used as an independent technique.

## 2. Experimental details

The investigated Au films were deposited onto 2 mm thick selected white float glass substrates (Präzisions Glas & Optic GmbH). Prior to this deposition, the substrates were wet chemical cleaned in a  $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 1:1$  solution at  $120^\circ\text{C}$  for 10 min, subsequently rinsed in de-ionized water and spin dried. Au films with  $d = 20$  nm were deposited by electron beam evaporation at a rate of 0.3 - 0.4 nm/s and a base pressure of  $< 10^{-6}$  torr, in the vacuum chamber of a LAB 500 evaporator (Leybold Optics GmbH). The deposition rate and film thickness were controlled by a standard oscillating quartz sensor.

The optical transmission and reflection of the films were measured with a Cary 5E (Varian Co.) spectrophotometer at normal incidence in the range 400 to 800 nm, with accuracies of 0.2 and 0.5%, respectively. A spectroscopic ellipsometer M44 (J. A. Woollam Co. Ins.) was employed for measurement of the ellipsometric angles ( $\psi$  and  $\Delta$ ) of the films. These ellipsometric parameters were measured for two angles of incidence,  $50$  and  $60^\circ$ , within the spectral region 400 - 800 nm.

## 3. Method for the determination of $(n, k, d)$ of the films

A short description of the method used for the determination of  $(n, k, d)$  of the thin films is presented here. In fact, this method is only applicable when the following major assumptions are observed: a monochromatic plane wave of unit amplitude at normal incidence impinges upon a very thin optically homogeneous, isotropic film, bounded by parallel surfaces. The film is supported by an optically homogeneous, isotropic, semi-infinite, slightly absorbing substrate of refractive index  $n_s$ . The two media are surrounded by air with a refractive index  $n_0 = 1$ .

The optical behaviour of such a film is described by its  $2 \times 2$  characteristic matrix [5]. The nanothickness of the film allows us to make a limited development of the matrix elements as a function of  $\tilde{n}d/\lambda$ . Retaining the terms up to fourth order, we obtain expressions for  $T_f, R_f, R'_f$ . The use of the relations  $(1 + R_f)/T_f, (1 - R_f)/T_f$  and  $(1 - R'_f)/T_f$  leads to a set of three equations, which are simpler than those for  $T_f, R_f, R'_f$  and can be easily solved numerically for the complex permittivity ( $\varepsilon$ ) and  $d$  of the film:

$$\frac{1 + R_f}{T_f} = \frac{(0.5\varepsilon_2^2 + \varepsilon_1^2 - \varepsilon_2^2\varepsilon_1 + 0.5\varepsilon_2^2n_s^2 - \varepsilon_1n_s^2 + \varepsilon_1^2n_s^2 + \varepsilon_1^3)\omega^4d^4}{6n_s} + \frac{(\varepsilon_2n_s - n_s\varepsilon_2\varepsilon_1)\omega^3d^3}{3n_s} + \frac{[(1 - \varepsilon_1)(n_s^2 - \varepsilon_1) + \varepsilon_2^2]\omega^2d^2}{2n_s} + \frac{2\omega d\varepsilon_2n_s + (n_s^2 + 1)}{2n_s} \quad (1a)$$

$$\frac{1 - R_f}{T_f} = \frac{\varepsilon_2^2\omega^4d^4}{6} + \frac{(\varepsilon_2n_s^2 - \varepsilon_2\varepsilon_1)\omega^3d^3}{3n_s} + \frac{\omega d\varepsilon_2 + n_s}{n_s} \quad (1b)$$

$$\frac{1 - R'_f}{T_f} = \frac{\varepsilon_2^2\omega^4d^4}{6} + \frac{(\varepsilon_2 - \varepsilon_2\varepsilon_1)\omega^3d^3}{3} + \omega d\varepsilon_2 + 1 \quad (1c)$$

where  $\varepsilon = \varepsilon_1 - i\varepsilon_2 = \tilde{n}^2 = (n - ik)^2$ ,  $\omega = 2\pi\lambda$  is the wave number.

To calculate  $(\varepsilon_1, \varepsilon_2, d)$ , we use the Levenberg-Marquart optimization routine. Eqs. (1a)-(1c) for  $\varepsilon$  and  $d$  are obtained for the case of an infinitely thick substrate. To analyse the influence of a

finite substrate (multiple reflections within it) and its optical performance (small spectral absorption), we manipulate the experimental data ( $R_{exp}, R'_{exp}, T_{exp}$ ), as in [6]. The transmittance and reflectance of the substrate -  $T_s$  and  $R_s$  - are measured and the refractive index ( $n_s$ ) and absorbance ( $a_s = \exp(-4\pi k_s d_s/\lambda)$ ) are calculated. Using ( $n_s, a_s$ ) and ( $R_{exp}, R'_{exp}, T_{exp}$ ) of a film deposited onto the finitely thick substrate, we evaluate ( $R_f, R'_f, T_f$ ) as functions of  $\lambda$  which enter Eqs. (1a) - (1c).

#### 4. Results and discussion

##### 4.1. Determination of ( $n, k, d$ ) of an Au film, by the proposed method

The Au films are measured spectrophotometrically, and ( $R_f, R'_f, T_f$ ) are obtained taking into account the finite substrate thickness. Then, we calculate ( $n, k, d$ ) for the Au film, solving Eqs. (1a) - (1c). We call this way of calculation the " $(R, R', T)$  method". The spectral dependence of  $n$  and  $k$ , determined in this way, are plotted in Fig. 1. The calculated thickness is  $d = 28.9$  nm.

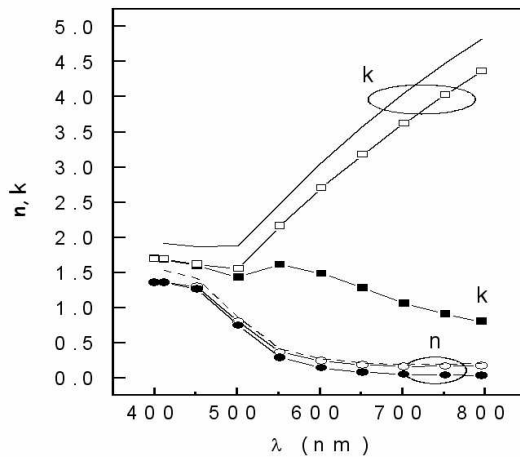


Fig. 1 Dispersion of  $n$  and  $k$  for an Au film:

- $n(R, T, d)$ , -○-  $k(R, T, d)$ ,
- $n(R, R', T)$ , -■-  $k(R, R', T)$ ,
- $n$  (VASE), —  $k$  (VASE).

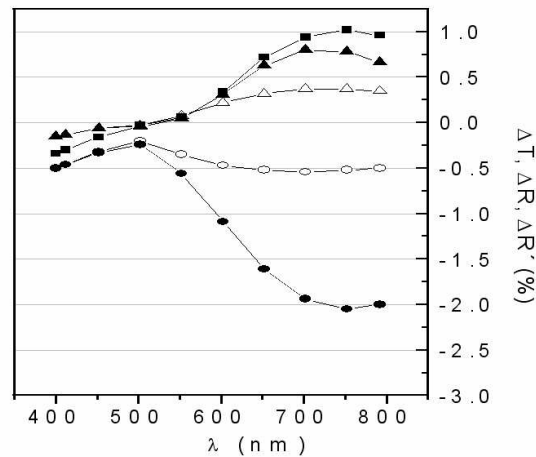


Fig. 2. Dispersion of  $\Delta T, \Delta R, \Delta R'$  for an Au film:

- $\Delta T(R, T, d)$ , -△-  $\Delta R(R, T, d)$ ,
- $\Delta T(R, R', T)$ , -▲-  $\Delta R(R, R', T)$ ,
- $\Delta R'(R, R', T)$ .

As a measure of the accuracy of the proposed method, we use the differences  $\Delta T = T_{cal} - T_f$ ,  $\Delta R = R_{cal} - R_f$  and  $\Delta R' = R'_{cal} - R'_f$ , where  $T_{cal}$ ,  $R_{cal}$  and  $R'_{cal}$  are the transmittance, front reflectance and back reflectance of the film, calculated with the obtained ( $n, k, d$ ), using exact Abelès matrix elements:  $T_f$ ,  $R_f$  and  $R'_f$  are the experimental data (after taking into account the finite thickness of the substrate). In Fig. 2, the dispersions of  $\Delta T$ ,  $\Delta R$  and  $\Delta R'$  are presented. The differences are too big for some wavelengths, for instance 2% in  $T$  and 1% in  $R'$  at  $\lambda = 750$  nm.

To decrease  $\Delta T$ ,  $\Delta R$  and  $\Delta R'$ , we modify the calculations. First, we calculate only  $d$ , using Eqs. (1a) - (1c). We accept this value for our further calculations (as if it was from an independent measurement). Then we calculate  $\epsilon_1$  and  $\epsilon_2$  values, using Eqs. (1a) and (1b). We call this method of calculation the " $(R, T, d)$  method". In Fig. 1, the spectral dependences of  $n$  and  $k$ , obtained using this method, are also plotted. In Fig. 2, the difference between  $T_{cal}$ ,  $R_{cal}$  and  $R'_{cal}$ , calculated with ( $n, k, d$ ) as obtained from the " $(R, T, d)$  method" and the experimental data ( $T_f, R_f$  and  $R'_f$ ) can be seen.  $\Delta T$ ,  $\Delta R$  and  $\Delta R'$  in this case decrease to the maximal uncertainty of the Cary 5E spectrophotometer.

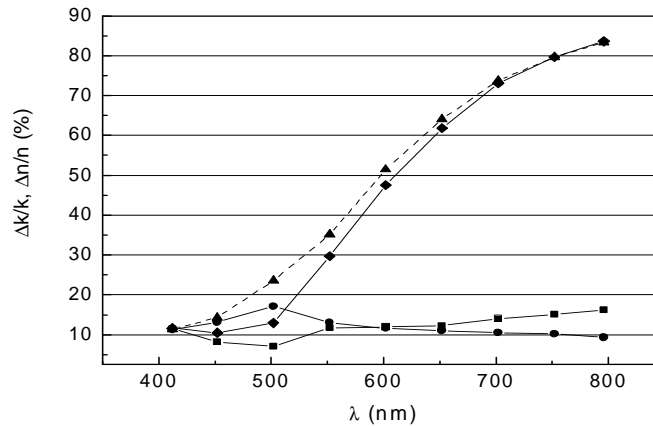


Fig. 3. Spectral dependence  $\Delta n/n$  and  $\Delta k/k$  for an Au film:  
 -■-  $\Delta n/n$ , (R, T, d), -●-  $\Delta k/k$ , (R, T, d),  
 -◆-  $\Delta n/n$ , (R, R', T), -▲-  $\Delta n/n$ , (R, R', T).

#### 4.2. Determination of $(n, k, d)$ of Au film by VASE

Additionally, VASE measurements have been performed on the Au film.  $\psi$  and  $\Delta$  are fitted using the effective media approximation (EMA) ( $n, k$  of bulk Au + voids). The optical constants for bulk Au are taken from the database of VASE, provided by J. A. Woollam Co. Ins. The film thickness, ( $d_{VASE}$ ), and the percent of the voids are fitted. The following results are obtained:  $d_{VASE} = 23.65$  nm,  $voids = 10.14$  % with a mean-squared error of 1.38.

The relative difference between  $(n, k, d)$  and  $(n_{VASE}, k_{VASE}, d_{VASE})$  are determined as:  $\Delta n/n = (n_{vase} - n)/n_{vase}$  and  $\Delta k/k = (k_{vase} - k)/k_{vase}$  and are plotted versus  $\lambda$ .

It can be seen that the use of the recalculated  $n$  and  $k$  from the "(R, T, d) method" decreases drastically the relative difference between  $(n, k)$  and  $(n_{VASE}, k_{VASE})$ . For instance,  $\Delta n/n$  decreases from 83% to 16% and  $\Delta k/k$  from 83% to 9% for  $\lambda = 800$  nm.

### 5. Conclusions

A new set of equations for the determination of  $(n, k, d)$ , based on limited development of the Abelès characteristic matrix up to fourth order is derived. This simple method for the evaluation of  $(n, k, d)$  was applied to thin evaporated Au thin films in the visible spectral region. An acceptable relative difference between these  $(\tilde{n}, d)$ , as compared to those obtained by the VASE technique has been achieved. The differences in  $(\tilde{n}, d)$ , obtained by the two methods, may be due to uncertainties in  $(\tilde{n}, d)$  evaluated by both methods, and is under investigation.

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