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Sensitivity and accuracy of new ellipsometric technique for the characterization of ultrathin films

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In this study the possibility for the improvement of accuracy of single wavelength measurements organized by multiple angle of incidence (MAI) null ellipsometry technique is shown. The "transparent film on transparent substrate" system in a range of 1.0–20.0 nm film thickness in the low-contrast region on the film-substrate surface was studied. The developed method allows an independent determination of the thickness and refractive index of an ultrathin transparent film under conditions of a strong correlation effect between these parameters.

Keywords: ellipsometry, accuracy, ultrathin films, thickness, refractive index

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INTRODUCTION

Ellipsometry is a valuable tool for studying ultrathin thermo-responsive polymer films that permits to record real-time sub-nanometer transformations in the structure of films during changes in the temperature of the liquid ambient [1, 2]. Thermo-responsive 'smart' coatings are able to change the affinity toward proteins and cells under temperature stimuli and therefore have potential applications in biology and medicine.

Molecular films are often single layers. They can be porous with a significant volume fraction containing ambient air. The ambient interface can be poorly defined, as surface coverage can be incomplete. Such films are called ultrathin to distinguish them from thicker films, which have a different optical behaviour [3, 4]. Ultrathin films have the thickness $d << \lambda / 2\pi n_f$, typically <15 nm in a dry state. Since the ellipsometric parameter Δ is the main parameter that varies for ultrathin films by traditional ellipsometric measurement, the two unknowns, d and n_f, are strongly correlated. One of possible ways to overcome the correlation problem was proposed in our earlier work [5]. Testing this method on the sensitivity and accuracy in the characterization of systems containing ultrathin thermo-responsive coatings is the main objective of this research.

EXPERIMENTAL

A commercially produced Null-ellipsometer LEF-3M, based on the optical scheme "polarizer–compensator–specimen-analyzer", with a He–Ne single-mode laser (light wavelength λ = 632.8 nm) was used as a light source to test the proposed method for the determination of measurement sensitivity and accuracy. The so-called four-zone technique was used to determine the polarization parameters (angles Ψ and Δ) for the light reflected from the sample surface. The light incidence angle φ varied between 55.5 and 57.5° with a step of 0.2°. This range of the φ angle corresponds to the region of the principal angle of incidence (where Δ ≈ π/2 or 3π/2) and thus ensures the maximal sensitivity.

The dependence between the incidence angle φ_0 and the film refractive index n_1 determined by the ($\delta\Psi = 0$) condition was obtained in an analytical form using the linear approximation

$$n_1 = n_2 \sqrt{\frac{2n_2^2\left(n_0'^2 - k_0'^2\right)tg^2\varphi_0 - \left(n_0'^2 - k_0'^2\right)^2\left(tg^2\varphi_0 + 1\right)}{n_2^4 tg^2\varphi_0 - \left(n_0'^2 - k_0'^2\right)^2}}, \quad (1)$$

where n'_0 and k'_0 are real and image parts of the complex refractive index N_0 of the virtual substrate modelling the real state of the substrate surface with a rough transition coating; n_2 is the refractive index of ambient; φ_0 is the incidence angle that satisfies the invariance condition for the amplitude ellipsometric parameter ($z = const$).

RESULTS AND DISCUSSION

It was shown [5] that the usage of a transparent substrate can significantly increase the sensitivity of an ellipsometric measurement and enables independence in determining the parameters of an ultrathin film. Taking measurements provided a constant amplitude ellipsometric parameter (Ψ = const) that allows to solve the problem of a strong correlation between the refractive index and the thickness of an ultrathin transparent film. The first task to achieve our goal was the development of an adequate model of a transparent substrate with a transition layer for an accurate description of the optical response of the system throughout the range of angles of incidence before and after the transparent film deposition. The ellipsometric properties of the real glass substrate in the vicinity of the principal angle of incidence are determined by the properties of the surface transition layer. Existence of this layer is caused by the heterogeneity of the surface and especially by its roughness. The real state of the glass surface can be modelled successfully using the conception of the so-called virtual substrate with the complex refractive index $N_0 = n'_0 - k'_0$ (Fig. 1) [5].

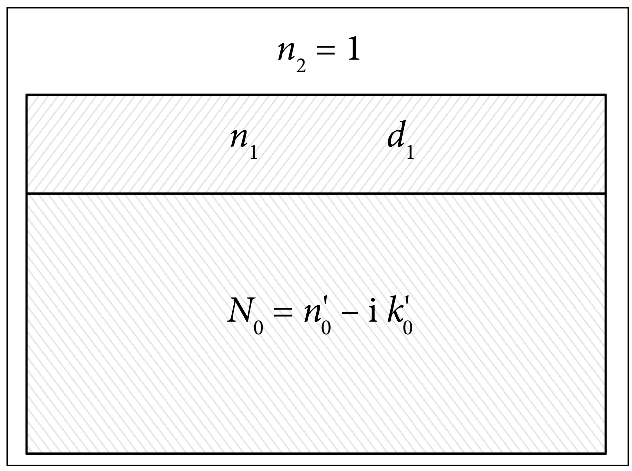

Fig. 1. A schematic view of a transparent ultrathin film with the parameters n_1 and d_1 on a transparent virtual substrate with the complex refractive index $N_0 = n'_0 - k'_0$ modelled in presence of a surface transition layer

Using of the null ellipsometry technique, which remains the most accurate in defining the parameters of elliptically polarized light [6, 7], is quite reasonable in view of the abovementioned facts. The linear dependence $\delta\Delta = Sd_1$ remains for the film thickness that significantly exceeds the applicability limit of the linear approximation (about 5 nm) if measurements are carried out for the angle of incidence determined by the Ψ = *const*-condition. Thus, one can conclude that the optical response of the system of glass substrate with a deposited ultrathin film ($d_1 \le 20$ nm) can be described within the linear approximation while the Ψ = *const*-condition is fulfilled. The linear relationship between the phase ellipsometric parameter Δ and the film thickness d_1 remains at a constant psi ($\delta\Psi = 0$) up to 20 nm thickness

$$\Delta - \Delta_0 = S d_1, \tag{2}$$

where $S = \frac{4\pi}{\lambda} n_2 \sin\varphi_0 \tan\varphi_0 \times \mathrm{Re}\left(\frac{N_0^2(n_1^2 - n_2^2)(n_1^2 - N_0^2)}{n_1^2(N_0^2 - n_2^2)(N_0^2 - n_0^2)\tan^2\varphi_0}\right)$ is the sensitivity coefficient of the phase ellipsometric parameter Δ to change of the film thickness, Δ_0 is the phase ellipsometric parameter of the pure substrate determined at the Ψ = *const*-condition. In other words, the amplitude ellipsometric ratio Ψ does not vary due to the deposition of a transparent film with the n_1 refractive index when the angle of incidence is equal to φ_0. As a result, the method is reduced to the determination of this angle φ_0. The accuracy in determination of the Ψ-parameter increases essentially and thus allows to independently determine the refractive index of an ultrathin film.

Therefore, the linear approximation for a simplified model in order to determine the transparent film parameters in the range of a low optical contrast and a strong correlation binding could be successfully used. The measurement procedure organized using the suggested method should be as follows:

1. From five to seven measurements are carried out before the deposition of a transparent film for the bare substrate in the vicinity of the principal angle of incidence ~56.5 ± 0.5° by the standard multiple angle of the incidence (MAI) method. The effective media parameters (n_0', k_0') as well as the angle dependence $\Psi_0(\varphi)$ are obtained for the bare substrate as a result of the standard fitting procedure.

2. After the film deposition, the method of measurement is reduced to determining of the incidence angle φ_0, at which the invariance condition Ψ = *const* is ensured. The search range for the incidence angle can be narrowed to 0.05 degree after 6–7 successive measurements. The exact value of the φ_0-angle is obtained after the numerical solution of the equation $\Psi_0(\varphi) = \Psi(\varphi)$.

3. The refractive index of the transparent film is determined using the analytical ratio (1) for the φ_0-value obtained previously. The sensitivity coefficient *S* is calculated within the suggested model.

4. The film thickness is calculated according to the inverse ratio (2).

The sensitivity and accuracy of the suggested method were also estimated. The refractive index error of the transparent film obtained within the technique suggested is determined by the ratio as follows:

$$\Delta n_1 = \frac{dn_1}{d\varphi}\Delta\varphi. \tag{3}$$

Here $\frac{dn_1}{d\varphi}$ is the derivative determined by the slope of $n_1(z)$-dependence (Fig. 2). The average value of the derivative is

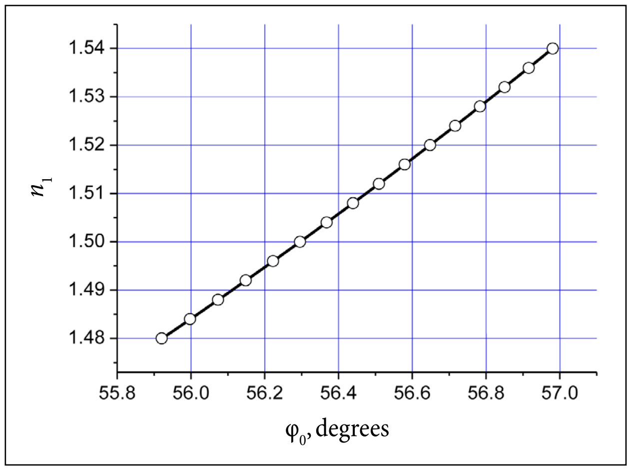

Fig. 2. The n_1 versus φ_0 dependences determined by the invariance condition of the amplitude Ψ-parameter. A continuous line is the dependence obtained using the analytical equation (1). The empty circles are the result of the optimization method using the exact Drude equation for the two-layer model

equal about 0.04 deg^{-1}. $\Delta\varphi = \frac{d\varphi}{d(\delta\psi)}\Delta(\delta\psi)$ is the error in determination of the incidence angle φ_0 at which the invariance condition Ψ = *const* is satisfied, $\frac{d\varphi}{d(\delta\psi)}$ is the derivative determined by the slope of $\delta\Psi(\varphi)$-dependence in the $\delta\Psi = 0$-region, $\Delta(\delta\Psi)$ is the error in determination of the $(\Psi_0 - \Psi)$-difference determined by the device sensitivity at the defined experimental conditions.

Experimental errors which occur at the ellipsometric measurements are defined by the smallest changes of ellipsometric parameters that can be measured for peculiar conditions [8]. These changes are the functions of the reflection coefficients

$$\delta\psi = k/R, \quad \delta\psi = \frac{kR}{R_p R_s}, \tag{4}$$

where $R = \sqrt{\frac{|R_s|^2 + |R_p|^2}{2}}$, R_s and R_p are the reflection coefficients for light polarized perpendicular and parallel to the plane of incidence, respectively, *k* is the coefficient that depends on the sensitivity of the device, which in our case is equal to 0.003 deg^{-1}. Thus in our case the experimental error of determination of the Ψ-parameter exceeds 0.01 deg and that of the Δ-parameter exceeds 0.5 deg.

As it can be seen from (4), the minimum change of the Ψ-parameter that can be registered in the operating range of the incidence angle is limited only by the hardware sensitivity that is ±0.01 deg. Therefore, the value of 0.02 deg was taken for the $\Delta(\delta\Psi)$-error. Consequently, dependence of the Δn_1-error on the film thickness as well as on the angle of incidence is mainly determined by the $\frac{d\varphi}{d(\delta\psi)}$-derivative dependence on these parameters. The calculation of the Δn_1-error value was carried out using (3) in dependence on the experimental conditions as well as on the film thickness for specimens with a different thickness of a transition layer. The results are shown in Fig. 3. The experimental conditions are determined by the angle of incidence that is strongly connected with the refractive index of the transparent film by (1) when the measurements are carried out using the technique suggested.

Evidently, the Δn_1-error increases sufficiently with the thickness decrease of the transparent film. The accuracy in the film refractive index determination reaches the maximum value in the region of the optical contrast absence, where $n_1 = n_0$. The $\delta\Psi(\varphi)$-dependences, having the maximal slope under the $n_1 = n_0$ condition, are the principal cause for this peculiarity $d(\delta\Psi)/d\varphi|_{n1 = n0} \rightarrow$ max. A slight Δn_1-error growth is also observed with decreasing the thickness of the transition layer. But the Δn_1-errors obtained in accordance with the suggested technique remain an order of magnitude smaller in comparison with the direct optimization method. The advantage is especially noticeable in the low contrast region between the film and substrate.

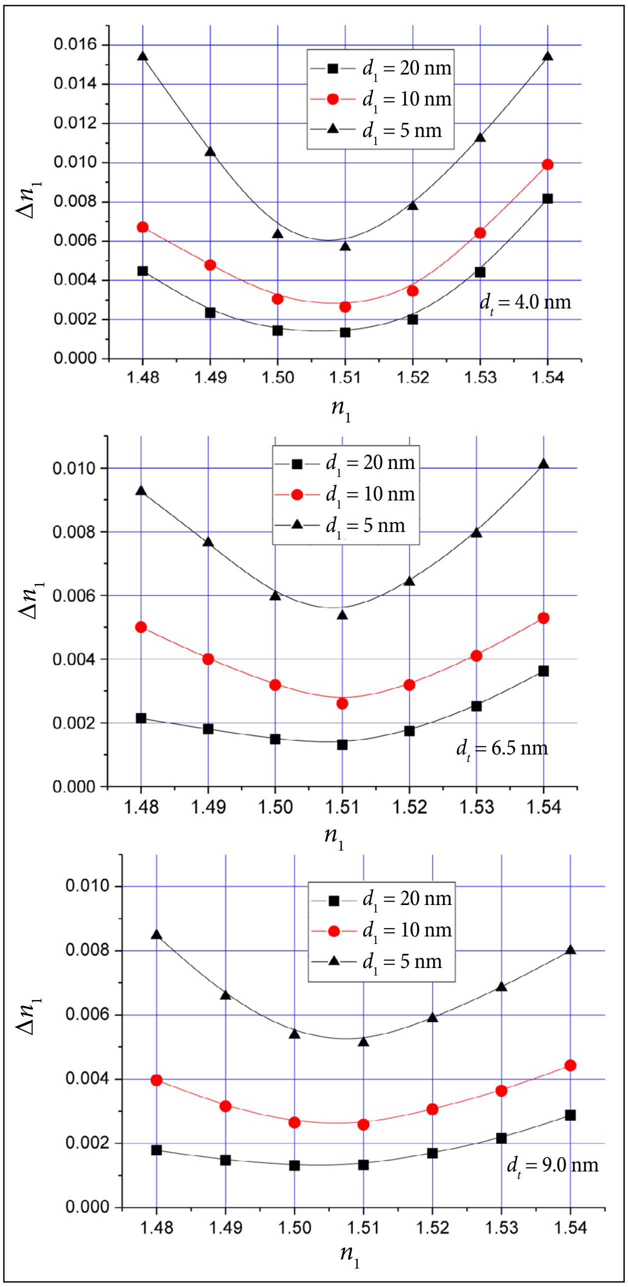

Fig. 3. The refractive index error in dependence on the experimental conditions $n_1(\varphi)$ and the film thickness d_1 for the substrate models with the refractive index $n_0 = 1.5152$ and a different thickness of the transition layer: a) $d_t = 4.0$ nm; b) $d_t = 6.5$ nm; c) $d_t = 9.0$ nm

The thickness error of the transparent film obtained within the technique suggested is determined not only by the accuracy in determination of the φ_0-angle of incidence, corresponding to the invariance condition of the Ψ-parameter, but also by the hardware sensitivity to the Δ-parameter change that varies considerably in the principal angle of the incidence region according to Eq. (4). Therefore, the Δd_1-error in the film thickness determination should be defined as the error of indirect measurements. Proceeding from Eq. (2), the error is defined by equality as follows:

$$\Delta d_1 = \sqrt{\left(\frac{d(d_1)}{dS}\Delta S\right)^2 + \left(\frac{d(d_1)}{d(\delta\Delta)}\Delta(\delta\Delta)\right)^2}. \qquad (5)$$

Here ΔS and $\Delta(\delta\Delta)$ are the errors in determination of the sensitivity coefficient S as well as in the phase parameter Δ change ($\delta\Delta = \Delta_0 - \Delta$), respectively. The ΔS-error is proportional to the above mentioned $\Delta\varphi$-error in determination of the φ_0 angle of incidence. The proportionality factor is determined by the slope of $S(\varphi)$-dependence (Fig. 4).

The $\Delta(\delta\Delta)$-error is determined by the hardware sensitivity, which reaches a maximum in the principal angle of incidence according to Eq. (4). The derivatives $\frac{d(d_1)}{dS} = \frac{\delta\Delta}{S^2}$,

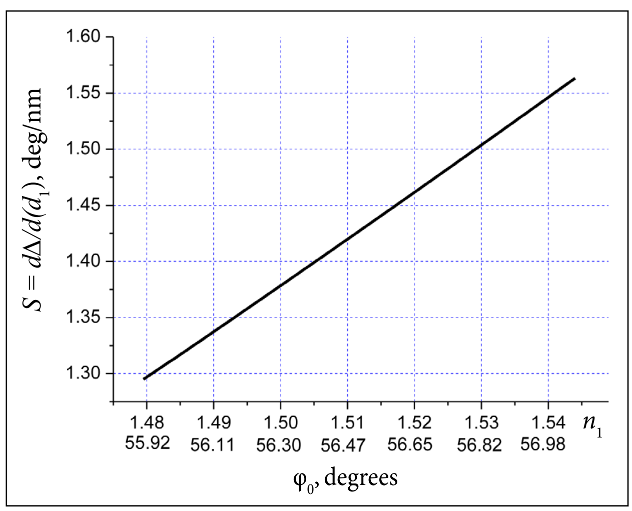

Fig. 4. Dependence of the sensitivity coefficient $S = d\Delta/d(d_1)$ on the film refractive index or the angle of incidence φ_0 determined on the $\Psi = const$-condition

$\frac{d(d_1)}{d(\delta\Delta)} = \frac{1}{S}$ are determined using the ratio (2). The first term in (5) does not depend on the thickness of transparent film because the $\frac{d(d_1)}{dS}$-derivative is directly proportional and the ΔS-error is inversely proportional to the film thickness d_1. The second term is by definition an invariant in relation to the thickness of the transparent film. Therefore, the results of calculation of the Δd_1-error are shown in Fig. 5 only for the particular thickness of a transparent film $d_1 = 10$ nm and depending on two parameters, namely: on the experimental conditions $n_1(\varphi)$ and on the properties of the transition layer d_f.

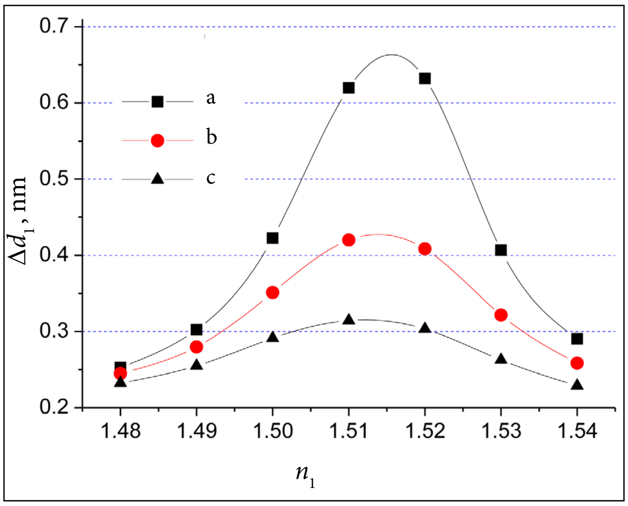

Fig. 5. The film thickness error in dependence on the experimental conditions $n_1(\varphi)$ for the substrate models with the refractive index $n_0 = 1.5152$ and a different thickness of the transition layer: a) $d_t = 4.0$ nm; b) $d_t = 6.5$ nm; c) $d_t = 9.0$ nm

The Δd_1-error grows in the region of the optical contrast vanishing ($n_1 \approx n_0$). It can be explained by the sensitivity decrease of the hardware output signal to the Δ-parameter variation in the region of the principal angle of incidence in accordance with (4). The hardware sensitivity to the Δ-parameter change decreases also in this region with the quality improvement of the substrate surface (decreasing of the transition layer thickness). It is the consequence of the amplitude reflection coefficient R_p decreasing while the surface quality improves and explains the Δd_1-error growing with decreasing of the transition layer thickness.

The presented results were obtained for the confidence intervals $\Delta(\delta\Psi)$ and $\Delta(\delta\Delta)$ designed for a single act of measurement according to (4). However, as it is known, confidence limits are narrowed with the number increasing of measurements in accordance with the law [9]

$$\varepsilon = t\sigma' / \sqrt{n}, \quad (6)$$

where t is the trust factor for the Student's t-distribution, which decreases with increasing of the measurements number n, σ' is the standard deviation of the single act of measurement characterising the concentration results relative to the center of distribution. Thus, the automation of the process in order to increase the number of measurements to 25 or 100 will narrow the confidence interval of 2 to 4 times, respectively.

The measurement technique suggested was tested in repeated studies of the modification processes of the glass surface using various coatings [10–13].

CONCLUSIONS

An original measurement technique as well as the method of experimental data processing are suggested for the system of "transparent film on transparent substrate" in a film thickness range of 1.0–20.0 nm. The error dependences of measured parameters on the experimental conditions and the structure of the substrate surface were obtained. It is shown that approaching of the surface structure to the ideal state (heterogeneity reduction associated with roughness) causes growth of errors. It was established that the reduction of the optical contrast between the film and the substrate leads to the reduction of accuracy in determining the thickness and more accurate measurement of the relative refractive index of the film that can be viewed as a kind of manifestation of the uncertainty principle.

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NAUJO ELIPSOMETRINIO METODO JAUTRUMAS IR TIKSLUMAS APIBŪDINANT ULTRAPLONUS SLUOKSNIUS

Santrauka

Darbe atskleista vieno bangos ilgio matavimų tikslumo pagerinimo galimybė, atliekama pagal nulinės elipsometrijos metodo daugybinį pasklidimo kampą. Siūlomas metodas verifikuotas sistemoje „skaidri plėvelė ant skaidraus padėklo“, kurioje sluoksnio storis kito 1,0–20,0 nm intervale. Tirta ir paviršiaus padėklas–plėvelė žemo kontrasto sritis. Sukurtas metodas leidžia savarankiškai nustatyti labai skaidrių plėvelių storį ir lūžio rodiklį, kai tarp šių parametrų egzistuoja stiprus koreliacijos efektas.