Optical-Refractometric Synthesis of Transmission Spectra and Optical Parameters of $0.5TiO_2 \cdot 0.5Nd_2O_3$ Thin Films

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Abstract

An original method for determining the optical parameters of thin films with the optical-refractometric synthesis of their transmission spectra is suggested. The proper choice of dispersion relation for refractive indices is substantiated. Experimental studies and computer simulations are performed for the quartz-glass optical element with $0.5TiO_2 \cdot 0.5Nd_2O_3$ film. The advantages of the suggested method are discussed.

Key words: thin film, transmission spectra, optical-refractometric synthesis, optical constants.

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Introduction

A variety of single- and multi-wave methods have been worked out in order to determine optical constants of a film deposited onto a substrate [1-3]. Ellipsometric techniques are the most precise among the single-wave methods[2,4]. Multi-wave methods are based on the Kramers-Kronig relations or the computer fitting of interference curves by means of Lorentz-or Drude-type dispersion relations, or their combination, for the refractive (n) and absorption (k) indices [3]. It should be noted that the application of the Kramers-Kronig dispersion relation is encumbered by a necessity of correct choice of reflection spectrum extrapolation in the low- and high-energy spectral ranges, as well as by requirements to the surface quality. The surface roughness noticeably affects the reflection spectra, especially in the ultraviolet range, which, in its turn, results in errors in the n and k determination.

Concerning the empirical and semi-empirical approaches enabling the experimentally observed dispersion of the refractive indices to be described, they can be classified according to the parameters included. Structural refractometric approach [5,6] is based on the analysis of various, mostly empirical, expressions for n and the density ρ and results in a number of rules, helpful for the calculation of optical constants. The optical dispersion studies have been further developed into the approach based on the concept of the "effective oscillator" and the "dispersion energy" by Wemple and DiDomenico [7,8]. A new approach to these problems has been formulated in Ref. [9,10], where optical and structural refractometric approaches are combined together. It is based on the so-called optical-refractometric (OR) relation, which is rather good obeyed for over 150 various nonmetallic materials (see, e.g., [11,12]):

$$\frac{\mu}{3\rho R(h\nu)} = \frac{1}{3}\frac{n^2(h\nu)+2}{n^2(h\nu)-1} = \left(\frac{\eta_s}{2}\right)^S \left(1+\frac{E_g^*}{E_{p\upsilon}}\right)^S - \left(\frac{h\nu}{E_s}\right)^S, \quad (1)$$

where s=2 for the intermediate part of the transparency range and s=3 for its high-energy part, E_g^* is the optical pseudogap, $R(h\nu)$ the molar refraction, and η_s and E_s the fitting parameters. The energy of the valence-electron plasma vibrations $E_{p\upsilon}$ is determined as [9,10]

$$E_{p\upsilon} = 28.82\sqrt{\frac{n_\upsilon \rho}{\mu}}, \quad (2)$$

where μ denotes the molar mass, n_υ the number of valence electrons per formula unit. Formula (1) describes the relation between n and E_g^* more precisely than the known Moss [13] and Wemple-DiDomenico [7,8] relations.

Here we propose a technique for obtaining optical constants of thin films, combining utilization of both the interference spectroscopic and the ellipsometric data, in which the OR relation is used as a dispersion relation for the film and the substrate refractive indices. The suggested method is applied to $0.5TiO_2 \cdot 0.5Nd_2O_3$ thin films, which represent promising materials for creating multi-layer dielectric coatings for the optical elements in laser engineering.

Experimental studies and computer simulations

We used $0.5TiO_2 \cdot 0.5Nd_2O_3$ thin films sputtered onto a quartz substrate for both interferential spectroscopic and ellipsometric measurements . The ellipsometric parameters were measured at the room temperature with the LEF-2M laser ellipsometer (λ=632.8 nm). The elaborated ellipsometric software enabled us to calculate the complex refractive index of the substrate ($N_2=n_2-ik_2$, with n_2 and k_2 being, respectively, the real refractive index and the absorption index of the substrate) and that of the film ($N_1=n_1-ik_1$, with n_1 та k_1 being, respectively, the real refractive index and the absorption index of the film), as well as the film thickness d, basing on the experimentally determined ellipsometric angles ψ and Δ at different incidence angles and a subsequent numerical solution of the main ellipsometric equation [2]

$$\rho = R_p/R_s = \tan\psi \cdot e^{i\Delta}, \quad (3)$$

where R_p and R_s are the reflectance coefficients for p- and s-polarizations, respectively. They are expressed through the Fresnel coefficients at the media boundaries

$$r_{01}^p = \frac{N_1\cos\varphi_0 - N_0\cos^*\varphi_1}{N_1\cos\varphi_0 + N_0\cos^*\varphi_1}, \quad (4a),$$

$$r_{12}^p = \frac{N_2\cos^*\varphi_1 - N_1\cos^*\varphi_2}{N_2\cos^*\varphi_1 + N_1\cos^*\varphi_2}, \quad (4b),$$

$$r_{01}^s = \frac{N_0\cos\varphi_0 - N_1\cos^*\varphi_1}{N_0\cos\varphi_0 + N_1\cos^*\varphi_1}, \quad (4c),$$

$$r_{12}^s = \frac{N_1\cos^*\varphi_1 - N_2\cos^*\varphi_2}{N_1\cos^*\varphi_1 + N_2\cos^*\varphi_2} \quad (4d),$$

as

$$R_p = \frac{r_{01}^p + r_{12}^p e^{-2i\beta}}{1 + r_{01}^p r_{12}^p e^{-2i\beta}}, \quad (5a),$$

$$R_s = \frac{r_{01}^s + r_{12}^s e^{-2i\beta}}{1 + r_{01}^s r_{12}^s e^{-2i\beta}}, \quad (5b)$$

where N_0 is the refractive index of the medium, φ_0 the angle of incidence at the medium-film boundary, φ_1 the angle of incidence at the film-substrate boundary, φ_2 the angle of incidence at the substrate-medium boundary, and $\beta=(2\pi/\lambda)dN_1\cos^*\varphi_1$ the phase thickness of the film. Provided that the ellipsometric parameters ψ an Δ have been determined for a chosen set of angles φ_0, the ρ_j values may be derived from Eq. (3) for the set of values (φ_{0j}, ψ_j, Δ_j). Having specified the initial values of the optical constants of the film n_1 and k_1, one can find the optical constants of the substrate n_2, k_2 and the film thickness d. The pair of the n_2 and k_2 values, obtained at this stage, serves as an initial approximation for the calculation of the film

optical constants. The process is being cycled until the self-consistent values of N_2 and N_1 or satisfactory precision of the calculated results are obtained.

The transmission spectra of the films at the room temperature were studied with the LOMO MDR-3 grating monochromator. The spectroscopic studies of the thin films result in an interferential transmission curve $T(\nu)$, where $\nu=1/\lambda$ is the wavenumber. For the thin films under test the condition $h\nu < E_g^*/2$ is kept valid. We may therefore apply the OR relation (Eq.(1)) with s=2 [9,10]. Having denoted

$$L(\nu) \equiv \frac{1}{3}\frac{n^2(\nu)+2}{n^2(\nu)-1}\ , \qquad (6)$$

one can write out the following system of three equations with respect to A, B, Q, coming from Eq. (1):

$$\begin{aligned} L_Q^{\max} &= A - B\cdot(\nu_Q^{\max})^2 \\ L_{Q+1}^{\max} &= A - B\cdot(\nu_{Q+1}^{\max})^2\ , \\ L_L &= A - B\cdot(\nu_L)^2 \end{aligned} \qquad (7)$$

where A and B represent the empirical fitting parameters in intermediate part of the transparency range, Q the assumed order of the interference maximum, and L_L and ν_L, respectively, the L value and the spectroscopic frequency at the laser wavelength. According to [14], the Q value is determined by a numeric solution of equations

$$\begin{aligned} L_Q^{\max} &= L_L + B\cdot\left[(\nu_L)^2 - (\nu_Q^{\max})^2\right] \\ L_{Q+1}^{\max} &= L_L - B\cdot\left[(\nu_L)^2 - (\nu_{Q+1}^{\max})^2\right] \end{aligned}, \qquad (8)$$

that take into account the known experimental values of the spectroscopic frequencies ν_Q, at which the interference maxima appear. If there happened a lack of experimental information for determining Q from the maxima, Q might be anyway calculated from the minima. Knowing the Q numbers and, correspondingly, the numbers of all the maxima and minima, we are able to calculate the exact values of the refractive index for all spectroscopic frequencies $\nu_Q^{\min}$ and $\nu_Q^{\max}$ from the relations

$$\begin{aligned} n_Q^{\max} &= \frac{Q}{2d\nu_Q^{\max}} \\ &\text{and} \\ n_Q^{\min} &= \frac{2Q+1}{4d\nu_Q^{\min}}. \end{aligned} \qquad (9)$$

Then, having plotted the $L=f[(h\nu)^2]$ or $L=f[(h\nu)^3]$ dependences, one can determine the intervals of linear smoothing in the intermediate (s=2) or high-energy (s=3) subranges of the transparency range, and so obtain the asymptotic approximations $L_2(h\nu\to 0)$ and the dispersion parameters B_2 (or L_3, B_3). Thus, within the given algorithm, the values of L ($h\nu$) are determined at the condition of rather precise ellipsometric measurements of the film thickness. Using the obtained L ($h\nu$) plots, one can finally calculate the refractive index from Eq.(6).

Results and discussion

The experimental transmission spectra $T_{\exp}(\lambda)$ (solid curves) for the thin $0.5TiO_2 \cdot 0.5Nd_2O_3$ films sputtered onto a quartz substrate are shown in Fig. 1. The refractive index n_L (see Table 1) measured with the ellipsometric technique and calculated for the laser wavelength, the film thickness d (see Table 1), together with the optical element transmission spectrum $T_{\exp}(\lambda)$, serve as the initial parameters for the calculations. The experimental transmission spectrum $T_{\exp}(\lambda)$ is used in order to obtain the spectral dependence of the absorption index $k(h\nu)$ by numerical solution of the equation

$$T_{\exp}(h\nu) = \tilde{\alpha}(h\nu)\frac{1-r_0(h\nu)}{1-R(h\nu)r_0(h\nu)}, \qquad (10)$$

where the second interface of the substrate [15] is taken into account in the right-hand side ($r_0(h\nu) = (n_0-1)^2/(n_0+1)^2$), and the values $\tilde{\alpha}$ are R given by the known expressions [14]. The software produced by us enables a reliable

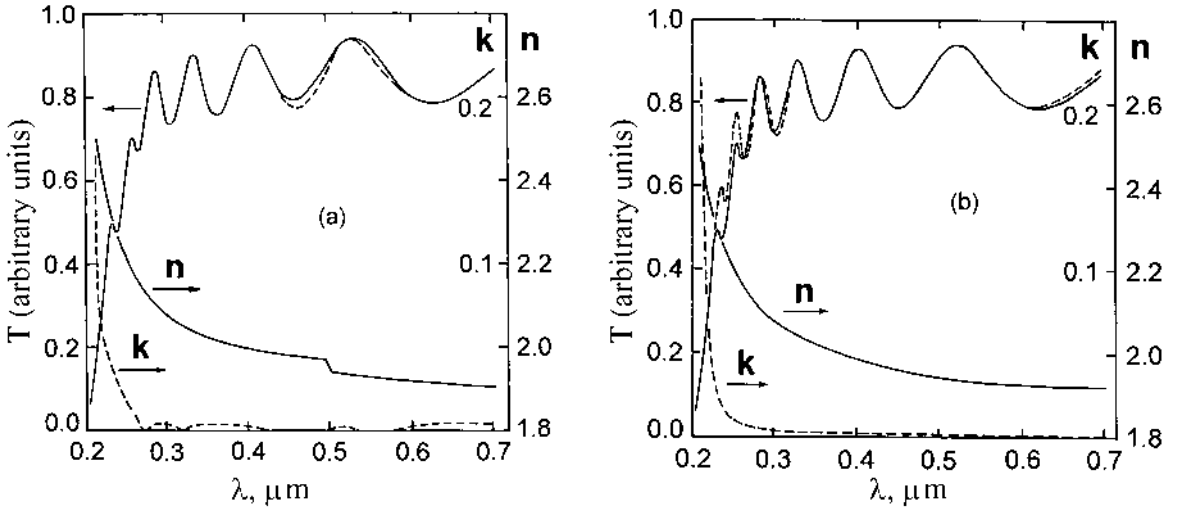

Fig. 1. Experimental (solid lines) and calculated (broken lines) spectral dependences of the transmission coefficient *T* and calculated dispersions for the refractive (*n*) and absorption (*k*) indices at the room remperature for $0.5TiO_2 \cdot 0.5Nd_2O_3$ thin film. The $T(\lambda)$, $n(\lambda)$ and $k(\lambda)$ dependences are calculated with the aid of the reversed synthesis (a) and the OR synthesis (b).

Table 1.

Ellipsometric (d, n_L, k_L) and interferential spectroscopic $(E_g^*, n_L^{OR}, k_L^{OR}, n_L^{synt}, k_L^{synt})$ parameters for the $0.5TiO_2 \cdot 0.5Nd_2O_3$ thin film on quartz substrate

d (μm)	E_g^* (eV)	w (meV)	n_L	n_L^{OR}	n_L^{synt}	k_L	k_L^{OR}	k_L^{synt}
0.4036	4.96	200	1.9138	1.9214	1.9214	3.4×10^{-5}	5.0×10^{-5}	1.2×10^{-3}

reversed synthesis of the transmission spectrum $T_{synt}(\lambda)$ (Fig. 1a) on the bases of the calculated $n(\lambda)$ and $k(\lambda)$ functions for the case of weakly absorbing layer [1]. Nevertheless, similarly to the method reported in [3], here the information on the chemical composition and the OR parameters of the film is missing, in spite of a satisfactory agreement of $T_{exp}(\lambda)$ and $T_{synt}(\lambda)$.

Besides the reversed synthesis, the software enables us to perform the OR synthesis of the transmission spectra $T_{OR}(\lambda)$ (Fig. 1b). In order to make the OR synthesis of $T_{OR}(\lambda)$, we should (i) apply the OR dispersion relation for the refractive index (see Eq.(1)) and (ii) work out the algorithm for separating the edge $k_{edge}(h\nu)$ and the background $k_{back}(h\nu)$ absorptions:

$$\begin{aligned} L_Q^{\max} &= L_L + B\cdot\left[(\nu_L)^2 - (\nu_Q^{\max})^2\right] \\ L_{Q+1}^{\max} &= L_L - B\cdot\left[(\nu_L)^2 - (\nu_{Q+1}^{\max})^2\right] \end{aligned}, \qquad (11)$$

where C and p are the parameters determined by the background absorption component smoothing in the transparency range, and w the characteristic energy obtained by a linear smoothing of the dependence

$$\lg\frac{\alpha_{edge}(h\nu)}{10^3} = \frac{1}{w}h\nu - \frac{E_g^*}{w}, \qquad (12)$$

with $\alpha_{edge}(h\nu)$ being the absorption coefficient in the range of the absorption edge. In frame of the suggested physical model, the background absorption $k_{back}(h\nu)$ is determined by the bulk extinction characterized by the parameter p. The latter is equal to 3, e.g., for the Rayleigh scattering ($I_{scat} \propto \lambda^{-4}$). The values of n_L^{synth} and k_L^{synth} calculated for the reversed synthesis, along with the E_g^*, w, n_L^{OR} and k_L^{OR} values are listed in the Table 1.

A comparison of the obtained results shows the OR synthesis of transmission spectra to possess a number of advantages with respect to the reversed synthesis. First, instead of the

spectrum computer adjustment, a physically reasonable model for the absorption index behaviour in the range of the optical absorption edge and in the transparency range of the films is suggested. The parameters, characterizing both the edge absorption (E_g^* and w) and the bulk extinction (C and p) are taken into account in this model, thus enabling to judge upon the degree of disorder in the thin amorphous (or crystalline) film and upon the nature of the bulk scattering in it. Finally, this information may be helpful in determining the film quality.

Second, the OR synthesis ensures not only a better fit of the calculated indices of refraction and absorption to the experimental ones (see Table 1 and Fig.1), but yields also in a physically reasonable dispersion behaviour of n^{OR} and k^{OR}. A slight difference between $T_{\exp}(\lambda)$ and $T_{\mathrm{OR}}(\lambda)$ in the range of the optical absorption edge is due to the structural disorder of thin films caused by a number of effects taking place in real thin films (deviation from stoichiometry, coexisting phases of different structures, intrinsic stresses, etc.).

Conclusions

A combined method for determination of the optical parameters of thin film, based on the ellipsometric (n_L, k_L, d) and interferential spectroscopic (the transmission spectrum $T_{\exp}(\lambda)$) data, is described. The OR relation, linking the refractive index, optical pseudogap and the plasma vibration energy for valence electrons, is used as a dispersion relation for the refractive index. An algorithm for the separation of the edge $k_{edge}(h\nu)$ and background $k_{back}(h\nu)$ absorptions is elaborated in framework of the proposed OR synthesis of transmission spectra. The advantages characteristic of the OR synthesis of transmission spectra are illustrated on the example of $0.5TiO_2 \cdot 0.5Nd_2O_3$ thin films.

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