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Research Article

Multi-angle spectrophotometry as a tool for determination of film parameters on single-layer structures

Nina S. Kozlova[1], Evgeniy A. Levashov[1], Philipp V. Kiryukhantsev-Korneev[1], Alina D. Sytchenko[1], Evgenia V. Zabelina[1]

1 National University of Science and Technology MISiS, 4-1 Leninsky Ave., Moscow 119049, Russia

Corresponding author: Nina S. Kozlova (kozlova_nina@mail.ru)

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Abstract

Ta–Si–C–N single-layer films have been synthesized by direct current magnetron sputtering on fused quartz substrates. The structural perfection of the films has been studied using X-ray diffraction, scanning electron microscopy and glow discharge optical emission spectroscopy. The optical parameters of the films have been studied using multi-angle spectrophotometry. The spectral dependences of the transmission coefficients of substrates and structures were measured for normal incidence of light in the wavelength range 200–2500 nm. We show that the transmittance spectrum of the specimen has an oscillating pattern due to interference phenomena that are typical for layered structures. The reflectance of the films and the substrates has been measured in the 200–2500 nm region for small incidence angles. The difference between the reflection coefficient at the maximum of the interference of the film and the corresponding reflection coefficient of the substrate at the same wavelength shows that the absorption in the film is low. A formula for determination of the film absorption index based on the measured parameters has been derived. The experimental and calculated data have been used for plotting the absorption spectra of the substrate, structure and film. Discrete refractive indices in the 400–1200 nm region have been calculated for reflections at two incidence angles by determining the positions of interference maxima in the reflectivity spectral responses. The results have been approximated using the Cauchy equation. The film thickness has been estimated to be $d_f = 1046$ nm ± 13%. The spectra of film extinction coefficients have been plotted with and without allowance for reflection. Obtained values of the refractive and absorption indices with and without reflection have been summarized in a table.

Keywords

multi-angle spectrophotometric methods, spectral transmittance, spectral reflectance, absorption index, refractive index, TaSiCN films

1. Introduction

Thin oxide films are currently widely used in the fabrication of structures for nano- and microelectronics devices, optoelectronics, acoustic electronics, microwave electronics as well as solar cells, optical and protective coatings in aircraft and space engineering etc. [1–6].

The key physical parameters that determine the properties of the films and their suitability for specific applications are [1, 2, 7–15]: film refractive index (n_f), film thickness (d_f) and film absorption, that is expressed through the absorption index (α_f, cm^{-1}) [16, 17] or the extinction coefficient κ_f [16, 18–20] which are in the following relationship:

$$\alpha_f(\lambda) = -\frac{\ln\left(T_f(\lambda)\right)}{d_f} = \frac{\kappa_f(\lambda)4\pi n_f}{\lambda}, \qquad (1)$$

where T_f is the spectra transmittance of the film, %; λ is the wavelength, nm.

Precision control of these parameters is of crucial importance for verifying whether synthesized films comply with the preset optical parameters of the final product [4]. This is especially difficult if the test film cannot be separated from the substrate [5]. Furthermore the measurements should be nondestructive [2] and hence require fast, reliable, simple and nondestructive techniques for measuring the optical parameters of thin films. Film thickness is evaluated by interferometric methods, profilometry, electron and atomic force microscopy [1]. Film thickness and refractive index are measured with nondestructive spectrophotometric methods. It has been reported [1, 4, 6, 13–15, 22–24] that both the refractive n index and the thickness of films can be retrieved by analyzing the maxima and minima in the spectra of film transmittance (T, %) or reflectance (R, %) originating from light interference in the plane-parallel layer (film). However film absorption measurements are a more complex task. Extinction coefficients of films were determined using the method of reciprocal tasks [5] and the waveguide mode excitation method [8].

The aim of this work is to develop nondestructive methods of multi-angle spectrophotometry for determining the optical parameters and thickness of films in film/substrate single-layer structures.

2. Experimental

The sputtering target having the composition $TaSi_2$ – 30% SiC was produced using the method of self-propagating high-temperature synthesis. The target was magnetron sputtered in DC mode in a 99,9995% N_2 atmosphere on a UVN-2M instrument [25] at $I = 2$ A, $U = 500$ V, residual and working pressure 0.005 and 0.2 Pa, respectively. The Pinnacle Plus power source (Advanced Energy, US) maintained the magnetron power at 1 kW. The coatings were deposited for 15 min. The substrates were quartz wafers. Before coating deposition the substrates were ultrasonically cleaned in isopropyl alcohol for 5 min on a UZDN-2T unit. Further Ar+ ion cleaning was carried out directly in the vacuum chamber for 2 min. The microstructure and elemental composition of the coatings were studied with scanning electron microscopy **(SEM)** under a Hitachi S-3400 microscope with a Noran 7 Thermo energy dispersive spectrometer. The element profiles were retrieved with a HORIBA-JY Profiler-2 glow discharge optical emission spectrometer. X-ray diffraction analysis was carried out on a D2 Phaser Bruker diffractometer in CuK_α radiation.

The spectral and angular responses of the transmittance and reflectance indices were measured at the Accredited Test Laboratory of Single Crystals and Stock on their Base of National University of Science and Technology MISiS on Agilent Technologies' Cary 5000 spectrophotometer with a universal measurement accessory **(UMA)**. The UMA combines a fixed light source, a 360 deg rotatable objective table and an independent detector moving through 10 to 350 deg in the horizontal plane about the objective table. This accessory allows to measure spectral and angular dependences of transmittance and reflectance in the 200–2500 nm region with a minimum step of 0.02 deg.

3. Results and discussion

The test specimens can be represented by a model of a single-layer structure consisting of a uniform film having the thickness d_f, the refractive index n_f and the absorption index α_f deposited onto a uniform substrate having the thickness d_{sub}, the refractive index n_{sub} and the absorption index α_{sub}. Schematic of the structure is shown in Fig. 1. A light beam propagates from the outer non-absorbing environment (air) having the refractive index $n = 1$.

Generally the energy interaction between the film/substrate structure and the incident light can be described by the following equation [16, 18, 26, 27]:

$$\Phi_0 = \Phi_T + \Phi_A + \Phi_S + \Phi_R, \qquad (2)$$

where Φ_0 is the radiation flux incident upon the specimen, Φ_T is the radiation flux having passed through the specimen, Φ_A is the radiation flux absorbed by the specimen, Φ_S is the radiation flux scattered by the specimen and Φ_R is the radiation flux reflected by the specimen.

In the case considered scattering can be ignored because of its negligibility and the overall system configuration. Then Eq. (2) can be rewritten as follows:

$$\Phi_0 = \Phi_T + \Phi_A + \Phi_R, \qquad (3)$$

All these parameters characterize the interaction between the material and the incident light rather than the properties of the material itself. Expressing these parameters in the form of the intensities we can proceed to the material's parameters:

$$1 = T + A + R, \qquad (4)$$

where T, A, R are the spectral coefficients of transmittance, absorption and reflectance, respectively.

The transmittance spectra of a typical structure T_{str} and a typical substrate T_{sub} for normal light incidence are shown in Fig. 2. It can be seen from Fig. 2 that the

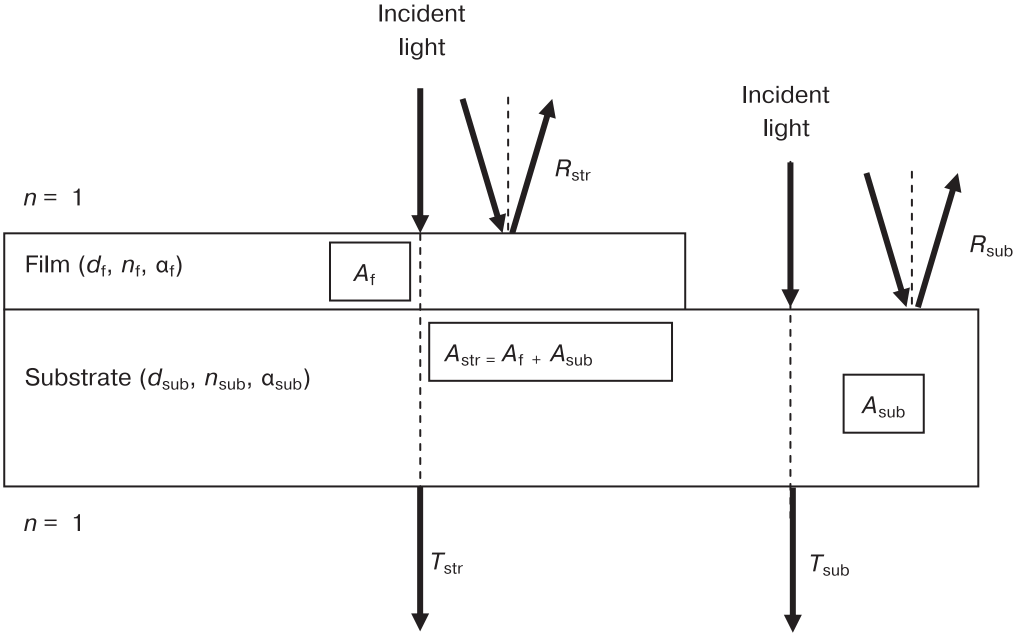

Figure 1. Model of a single-layer structure (film on substrate) and light interaction schematic.

transmittance spectrum of the specimen has an oscillating pattern due to interference phenomena that are typical for layered structures.

Measuring the reflectance of the structure R_{str} at the film side we can evaluate the absorption coefficient of the structure A_{str} using the formula [27]

$$A_{str} = 1 - T_{str} - R_{str}. \tag{5}$$

The results are shown in Fig. 2. It can be seen from Fig. 2 that the quartz substrate has a low absorption over the entire experimental range. The test specimen absorbs weakly in the IR region while in the visible region the absorption increases with decreasing wavelength.

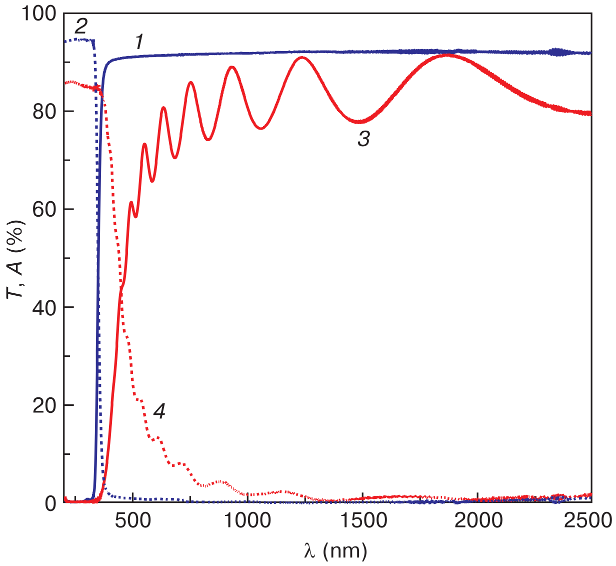

Figure 2. (*1* and *3*) Transmittance and (*2* and *4*) absorption spectra of (*1* and *2*) substrate and (*3* and *4*) typical structure.

In the simplest case without allowance for scattering and reflection Eq. (4) can be written as follows:

$$1 = A_{str} + T_{str}. \tag{6}$$

Then the absorption coefficient of the structure can be expressed as follows:

$$A_{str} = A_f + A_{sub}. \tag{7}$$

where A_f and A_{sub} are the absorption coefficients of the film and the substrate, respectively.

$$A_{str} = 1 - T_{str};\ A_f = 1 - T_f;\ A_{sub} = 1 - T_{sub}. \tag{8}$$

where T_f and T_{sub} are the transmittances of the film and the substrate, respectively.

The transmittance of the film can be derived from Eqs. (6)–(8):

$$T_f = 1 - T_{sub} + T_{str}. \tag{9}$$

The absorption coefficient of the film is determined using Eq. (1) which taking into account Eq. (9) can be transformed, and the following expression can be written for absorption without allowance for reflection:

$$\alpha_f = \frac{\ln \frac{1}{T_f}}{d_f} = \frac{\ln \frac{1}{1 - T_{sub} + T_{str}}}{d_f}. \tag{10}$$

The absorption index α with allowance for reflection is written as follows [28–30]:

$$\alpha = -\frac{\ln\left[\dfrac{T}{(1-R)^2}\right]}{d}. \tag{11}$$

Thus with allowance for reflection Eq. (10) can be transformed as follows:

$$\alpha_{\mathrm{f}} = -\frac{\ln\left(\dfrac{T_{\mathrm{f}}}{(1-R_{\mathrm{str}})^2}\right)}{d_{\mathrm{f}}} = -\frac{\ln\left(\dfrac{1-T_{\mathrm{sub}}+T_{\mathrm{str}}}{(1-R_{\mathrm{str}}^2)}\right)}{d_{\mathrm{f}}}. \tag{12}$$

The transmittances of the substrate and the structure and the reflectance of the structure at the film side can be measured with a spectrophotometer. Our measurement results are shown in Fig. 3. However the film thickness is unknown.

The thicknesses and the refractive indices of the films can be calculated using the spectrophotometric method of reflection at two angles of incidence [15]. This method is only applicable to the spectral region in which the film is transparent or its absorption is sufficiently low for being neglected. The higher the absorption of the film the greater the difference between the film reflectance at the maximum interference and the substrate reflectance at the same wavelength. For finding this region, reflectance spectra of the film and the substrate were measured at a 10 deg incidence angle (Fig. 4).

The reflectance spectra of the specimens (Fig. 4) clearly show extrema originating from the interference of the two beams reflected from the environment/film and the film/substrate interfaces. For the test specimen the two incidence angle reflection method is only applicable at above 425 nm because the absorption is the lowest in this region.

To evaluate the refractive index of the deposited layer we used the reflectance spectra for two non-polarized light incidence angles, i.e., $\varphi_1 = 10$ deg and $\varphi_2 = 20$ deg.

First of all refractive indices are measured. To do this, the wavelengths $\lambda\varphi_1$ and $\lambda\varphi_2$ corresponding to the same interference extremum for each interference extremum are selected on the obtained spectra. Then the film refractive index for the narrow wavelength range $\lambda\varphi_1 - \lambda\varphi_2$ was determined using the formula

$$\left(\frac{n_{\mathrm{f}}}{n}\right)^2 = \frac{\sin^2\varphi_1 - \beta\sin^2\varphi_2}{1-\beta}, \tag{13}$$

where β is the coefficient determined as follows:

$$\beta = \left(\frac{\lambda_{\varphi 1}}{\lambda_{\varphi 2}}\right)^2. \tag{14}$$

The final value of the film refractive index is calculated using the following equation:

$$n_{\mathrm{f}} = \sqrt{\left(\frac{\sin^2\varphi_1 - \beta\sin^2\varphi_2}{1-\beta}\right)}. \tag{15}$$

As a result of the calculations we obtain a discrete array of refractive indices. The dispersion dependence of the refractive index is determined by approximating the calculated data using e.g. the Cauchy equation as follows:

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}, \tag{16}$$

where A, B and C are material constants.

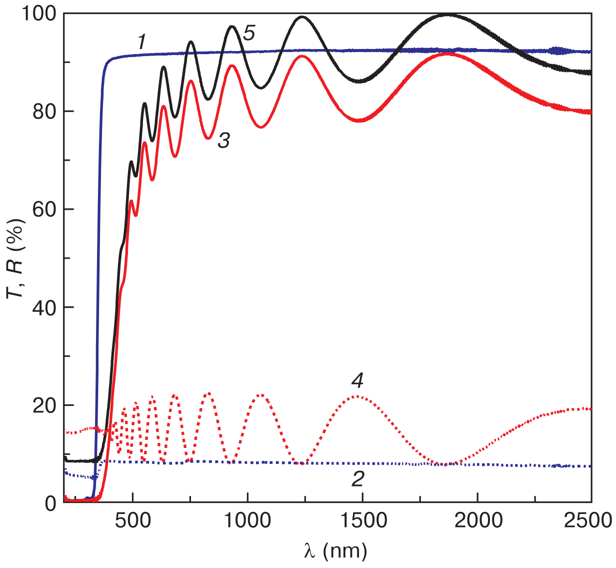

Figure 3. (*1*, *3* and *5*) Transmittance and (*2* and *4*) reflectance spectra of (*3* and *4*) typical structure, (*1* and *2*) substrate and (*5*) film.

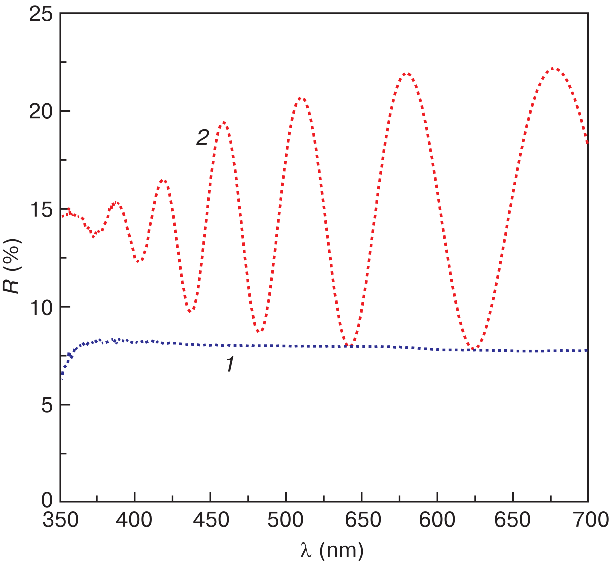

Figure 4. Light reflection measurement data for 10 deg incidence angle on specimen taken at (*1*) fused quartz substrate side and (*2*) film side.

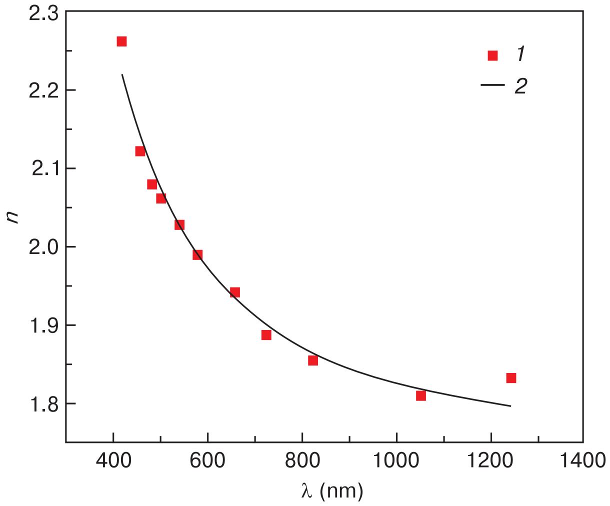

Figure 5. Dispersion dependence of refractive index of typical specimen: (*1*) data obtained by calculation using Eq. (16) and (*2*) Cauchy approximation.

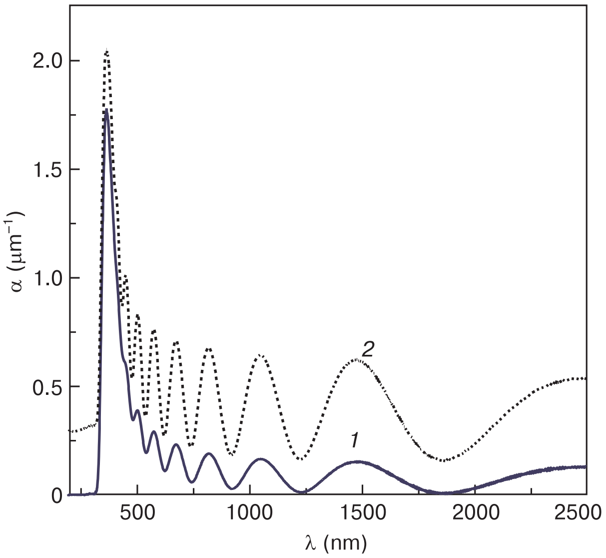

Figure 6. Film absorption spectra (*1*) without and (*2*) with allowance for reflection.

The optical thickness of the film ($d_f \cdot n_f$) is determined using the following formula:

$$d_f n_f = \frac{\lambda_1 \lambda_2}{k(\lambda_2 - \lambda_1)}, \tag{17}$$

where λ_1, λ_2 are the wavelengths of adjacent interference extrema in the interference response taken at one incidence angle, nm; and k is a coefficient which takes on 2 if two adjacent maxima are taken or 4 if adjacent maximum and minimum are taken.

With allowance for the film refractive index obtained using Eq. (15) the film thickness can be calculated as follows:

$$d_f = \frac{\lambda_2 \lambda_1}{k n_f (\lambda_2 - \lambda_1)}. \tag{18}$$

The refractive index evaluation results obtained using the reflection spectrophotometric method for two incidence angles and their approximation results obtained using the Cauchy equation (Eq. (16)) are shown in Fig. 5 for the transparent film of the specimen. The film thickness of the specimen as determined using Eq. (18) was d_f = 1046 nm ± 13%. The absorption spectra with and without allowance for reflection obtained using Eqs. (10) and (12), respectively, are shown in Fig. 6. The summarized data on the refractive and absorption indices of the specimens are shown in Table 1.

4. Conclusion

Ta–Si–C–N single-layer films were synthesized by magnetron sputtering on fused quartz substrates. The structural perfection of the films was studied using X-ray diffraction, scanning electron microscopy and glow discharge optical emission spectroscopy.

The 200–2500 nm transmittance spectra of the structures and the fused quartz substrates for normal light incidence and the reflectance spectra at 10 and 20 deg incidence angles were measured using multi-angle spectrophotometry.

A formula for determination of the film absorption coefficient based on the measured parameters was derived. The experimental and calculated data were used for

Table 1. Refractive and absorption indices with and without allowance for reflection for a typical specimen in the 450–1200 nm region

λ (nm)	***n***	**A_f (μm⁻¹)**	
		With allowance for reflection	**Without allowance for reflection**
450	2.153	0.603	0.959
500	2.075	0.367	0.744
550	2.018	0.192	0.391
600	1.974	0.222	0.553
650	1.940	0.157	0.471
700	1.913	0.191	0.580
750	1.891	0.057	0.221
800	1.873	0.160	0.591
850	1.858	0.161	0.578
900	1.846	0.054	0.244
950	1.835	0.041	0.237
1000	1.826	0.116	0.495
1050	1.818	0.160	0.629
1100	1.812	0.138	0.544
1150	1.806	0.075	0.345
1200	1.801	0.022	0.188

plotting the absorption spectra of the substrate, structure and film, with and without allowance for reflection.

Using experimental methods based on the measurement of interference extrema in the reflectance spectra, the film thickness was estimated to be $d_{f.}$ = 1046 nm ± 13 %, and discrete film refractive indices were obtained. The results were approximated using the Cauchy equation.

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