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Optical properties of thin films of titanium with transient layers on them

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Abstract. Within the Beattie spectroellipsometric method, we measured the ellipsometric parameters of thin Ti films deposited onto glass substrates by magnetron sputtering in argon atmosphere. Measurements were carried out at five angles of incidence with light from the visible and ultraviolet ranges of the spectrum. Using the Airy recurrent formulas, we solved the inverse problem of ellipsometry for a three-layer model of films. The model includes nine unknown quantities – three thicknesses of layers and six optical constants, namely: the refractive and absorption indices of all these layers. The results obtained show that the upper layer being in contact with air consists of titanium oxide of the TiO_2 type, the second layer is made of pure metallic titanium, and, finally, the third layer adjoining the glass substrate is also oxide TiO_2. It is worth noting that the optical constants of the second layer are practically identical to those of massive Ti. The calculations of the film thicknesses and optical constants by using the one-layer model gave the values significantly different from the optical constants of massive titanium. In addition, the studies of both the electric conductance of the prepared Ti films and morphology of their surface with an atomic force microscope were carried out.

Keywords: thin films, titanium oxide, optical constants, three-layer model, spectral ellipsometry.

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1. Introduction

Thin films of titanium deposited on glass, silica, and other dielectric substrates under not ultrahigh vacuum possess a transient surface layer from the side of vacuum (air), as well as from the side of a substrate. Mainly, they are titanium oxides of the type of TiO_2, Ti_2O_3, or TiO. Films of titanium are widely used as coatings in various technical units, as absorbers of gases in high-vacuum pumps, etc. The films of TiO_2 have found wide application in solar cells [1]. Optical properties of thin metal films are determined by spectrophotometric, interferometric, and spectroellipsometric methods. In the latter case, the optical constants n (refractive index) and κ (absorption index) are given by the Airy formulas for a uniform planar layer [2] or by a number of approximate formulas [3] deduced on the basis of the Airy formulas. Optical constants determined in such calculations are significantly different in various works and, in addition, differ essentially from the corresponding optical constants of massive metals by their values [3-5]. In the present work, we use a more real model, namely, the three-layer model of a thin Ti film.

2. Experimental

We sprayed thin films of titanium with various thicknesses on glass substrates by using the magnetron sputtering under a constant current in argon at the pressure $P = 0.66\,\text{Pa}$. The sputtering chamber was preliminarily evacuated down to the pressure $P = 1.3 \times 10^{-3}\,\text{Pa}$, and then it was filled with argon. A glass substrate was heated to a temperature of 150 °C. The produced films of titanium were measured in air. Therefore, we consider the three-layer model of a film (Fig. 1).

The upper layer 1 is a layer consisting of oxide and adsorbed molecules. The middle layer 2 is metallic titanium, and the lower layer represents the glass-

titanium interface arising as a result of chemical reactions between molecules of glass and titanium. The lower layer is responsible for the adhesion of a Ti film. The task consisted in the determination of the optical constants and the thicknesses of all three layers. That is, it is necessary to find nine unknown values. Within the Beattie method [6], we measured such ellipsometric parameters as the azimuth of a recovered linear polarization Ψ and the phase shift between the *p*- and *s*-components of a reflected light wave Δ for a number of wavelengths in the visible and ultraviolet spectral ranges. The measurements were performed at five angles of light incidence onto a film. Then, by using the Airy recurrence formulas [2], we solved the inverse problem of spectroellipsometry numerically by using the program MATLAB with the Curve Fitting Tool subprogram.

The relevant recurrence formulas take the form

$$R_j^{p,s} = \frac{r_j^{p,s} + R_{j+1}^{p,s} e^{2iG_i}}{1 + r_j^{p,s} \cdot R_{j+1}^{p,s} e^{2iG_i}},\ j=1, 2, 3, 4, \qquad (1)$$

where $r_j^{p,s}$ are the Fresnel amplitude coefficients of reflection,

$$r_j^p = \frac{\tilde{n}_j \cdot \cos\varphi_{j-1} - \tilde{n}_{j-1} \cos\varphi_j}{\tilde{n}_j \cdot \cos\varphi_{j-1} + \tilde{n}_{j-1} \cos\varphi_j}, \qquad (2)$$

$$r_j^s = \frac{\tilde{n}_{j-1} \cdot \cos\varphi_{j-1} - \tilde{n}_j \cos\varphi_j}{\tilde{n}_{j-1} \cdot \cos\varphi_{j-1} + \tilde{n}_j \cos\varphi_j}, \qquad (3)$$

$$G_j = 2\pi \tilde{n}_j d_j \frac{\cos\varphi_j}{\lambda}, \qquad (4)$$

$$\frac{R_1^p}{R_1^s} = \mathrm{tg}\,\psi \cdot e^{i\Delta}. \qquad (5)$$

In relations (1) to (5), λ is the light wavelength, d_j is the thickness of the corresponding layer (see Fig. 1), φ_0 is the angle of light incidence on the film from the side of air, and $\tilde{n}_j$ is the complex-valued refractive index of the *j*-th layer, $\tilde{n}_j = n_j + i\kappa_j$. Here, n_j is the real refractive index of the *j*-th layer, and κ_j is the absorption index of the corresponding layer. The refractive index of air , and the refractive index of glass $n_4 = 1.52$. The corresponding refraction angles φ_j can be expressed in terms of n_0, φ_0 and $\tilde{n}_j$ by the Snell law. In relation (1), $R_4^{p,s} = r_4^{p,s}$. We also measured the electric conductance of all the specimens with a Wheatstone bridge and studied morphology of film surfaces with an atomic force microscope NT-MDT.

3. Results and discussion

By performing the ellipsometric measurements and the relevant calculations for five Ti films with different thicknesses, we obtained the following results. The layer 1 in Fig. 1 is mainly composed of TiO_2 molecules. The same is true for the layer 3 between the film and the glass substrate. In Table 1, we present values of n_1 and κ_1 of the first layer for one of the Ti films under study and also n_3 and κ_3 of the third layer. The thicknesses of layers for this specimen are as follows: $d_1 = 2.4$ nm, $d_2 = 14.2$ nm, and $d_3 = 2.2$ nm. The comparison of data in Table 1 with the results given in [7] for crystallline TiO_2 testifies to their good quantitative agreement. Moreover, the dispersions show the similar course.

For the layer 1, we calculated the absorption coefficient $K = \frac{4\pi\kappa}{\lambda}$ and constructed a plot of its dependence on λ which is given in Fig. 2. As seen from Fig. 2, the absorption coefficient begins to increase, by starting from $\lambda \sim 400$ nm, and reaches the maximum near $\lambda \sim 300$ nm. Using the data obtained for the first layer, we calculated the spectrum of transmission for the specimen 10 μm in thickness. In the first approximation,

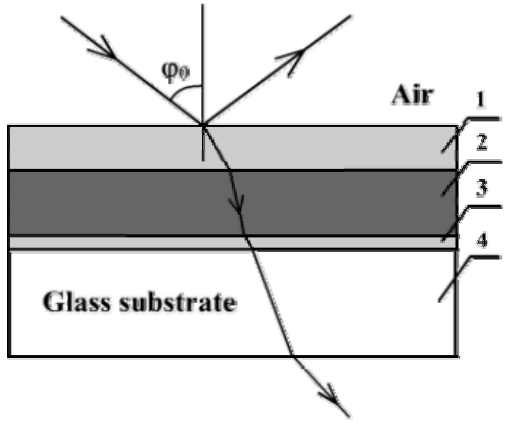

Fig. 1. Three-layer structure of a thin Ti film.

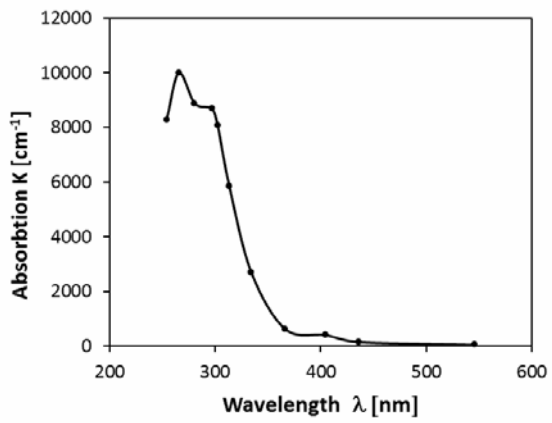

Fig. 2. Spectral behavior of the absorption coefficient K of the oxide layer (1).

Table 1. The values of *n* and κ for one of these Ti films.

λ, nm	546.1	435.8	404.7	366.3	334.1	313.1	302.1	296.7	280.4	265.2	253.6
n_1	2.76	2.92	3.06	3.47	3.82	3.87	3.83	3.81	2.71	2.19	2.08
κ_1	0.018	0.05	0.13	0.18	0.714	1.46	1.94	2.05	1.98	2.11	1.67
n_3	2.85	2.96	3.19	3.57	3.98	3.94	3.88	3.93	2.85	2.22	2.01
κ_3	0.017	0.075	0.17	0.23	0.88	1.88	2.08	2.09	1.99	2.08	1.7

Table 2. The results obtained for the layer 2 together with data for massive titanium [7].

λ, nm	546.1	435.8	404.7	366.3	334.1	313.1	302.1	296.7	280.4	265.2	253.6
n_2	1.64	1.53	1.33	1.19	1.05	0.92	0.91	0.91	1.08	1.09	1.15
κ_2	2.51	2.29	2.17	2.07	1.99	1.65	1.54	1.48	1.34	1.2	1.16
n_m	1.86	1.65	1.57	1.38	1.17	1.04	1.04	1.05	1.14	1.17	1.22
κ_m	2.56	2.23	2.16	2.07	1.9	1.65	1.52	1.45	1.33	1.26	1.22

we can neglect multiple reflections, which allows us to get the formula of the coefficient of transmission T_0 at the normal incidence,

$$T_0 = (1 - R_0)e^{-Kd}, \tag{6}$$

where R_0 is the reflection coefficient at the normal incidence.

For this specimen, the results of calculations are shown in Fig. 3. A completely analogous spectral behavior of the transmission for thin TiO_2 films was also measured in [8]. As seen from Fig. 3 and by data from [8], the transmission is practically absent near $\lambda \sim 300$ nm. The results for layer 3 are analogous to those shown in Figs 2 and 3. Thus, we may conclude that both layer 1 and layer 3 are titanium oxides of the TiO_2 type.

In Table 2, we present the results obtained for layer 2 together with data for massive titanium [7].

As seen from Table 2, the absorption index κ of the layer 2 practically coincides in the limits of errors with the absorption index κ of massive titanium. At the same time, the refractive index *n* of layer 2 is somewhat lower than *n* of massive titanium. The latter fact can be explained by the active absorption of molecules of gases by the films of titanium, especially at high temperatures (titanium superhigh-vacuum pumps). But, even at room temperature, they well absorb atoms and molecules of hydrogen. It is this fact that can explain somewhat lower values of the refractive index of layer 2 as compared with that of massive titanium. Thus, in view of the data presented in Table 2, we may conclude that the layer 2 is metallic titanium. By the way, the calculations performed for this specimen at $\lambda = 546.1$ nm by using the one-layer model gave the following results: $n = 2.02$, $\kappa = 2.08$, $d = 16$ nm. As seen, these values are significantly different from data for massive titanium and values obtained within the three-layer model. For the specimen under study, we measured also its resistance: $R = 1250$ Ohm. This value yields the specific resistance for a film of this specimen $\rho = 2.79 \times 10^{-5}$ Ohm · m and the specific conductivity $\sigma = 3.59 \times 10^4$ Ohm^{-1} · m^{-1}. For massive titanium, the specific resistance $\rho_m = 5 \times 10^{-7}$ Ohm · m, i.e., it is less by two orders. The latter fact can be explained by two reasons. The first one is presence of the oxide layer TiO_2 with the thickness $d = 2.4$ nm on the layer of metallic titanium, and the second reason is related to the size effects in thin films [9]. According to the Fuchs theory [9], the following approximate formula is valid at the diffusive reflection from boundaries of a film:

$$\frac{\sigma}{\sigma_0} = 1 - \frac{3}{8\alpha}, \tag{7}$$

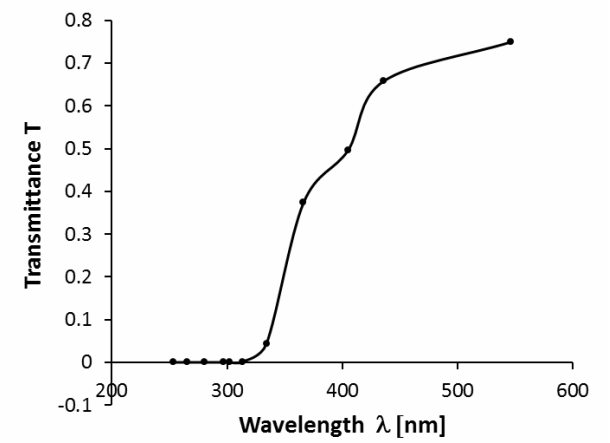

Fig. 3. Spectral behavior of the coefficient of transmission for the specimen 10 μm in thickness.

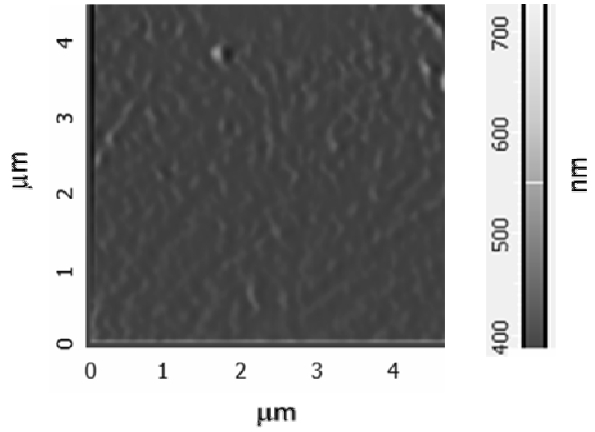

Fig. 4. AFM image of Ti film surface.

where σ is the film conductivity, σ_0 is the conductivity of massive metal, $\alpha = d/l$, d is the film thickness, and l is the free path length of an electron. Using the data obtained by us, we calculated the free path length $l = 37.2$ nm for a titanium film. By the order of magnitude, this value coincides with the results for other metals [9]. Thus, we can draw a conclusion that the three-layer model applied by us to Ti films describes the real situation significantly better than the one-layer model. For the other titanium films with various thicknesses, we got results analogous to the above-discussed ones. A single specific feature is as follows: the less the film thickness, the larger the difference of the refractive indices of the layer 2 and metallic titanium as compared with such a difference for the above-considered specimen. This supports once more the conclusion about the absorption of gases by Ti films during the spraying. Indeed, for thinner films, the absorption must have a greater influence on the refractive index due to a higher concentration of gases in a film.

In Fig. 4, we present the AFM image of the surface of the Ti film under study.

Fig. 4 indicates that the film is not fully homogeneous. Thus, the three-layer model used in this work is some approximation. But the results obtained by us have demonstrated that this approximation is sufficiently suitable and works significantly better than the one-layer approximation.

4. Conclusions

1. It is shown that Ti films obtained under not superhigh vacuum and introduced into the air atmosphere are coated by a TiO_2 layer from their top. The same layer of TiO_2 is located between the metallic film and the glass substrate.
2. The optical constants of a Ti film calculated by the three-layer model are practically identical to those of massive titanium.
3. The three-layer model of a Ti film corresponds to real situation to a greater extent than the one-layer model.

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