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STUDY OF MECHANISMS OF LIGHT ABSORPTION IN TITANIUM DIOXIDE FILMS

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This work is devoted to comparison of optical absorption value of titanium dioxide coatings obtained by means of reactive thermal evaporation (RTE) and its activated species (ARTE), as well as to study on the dependence of the absorption coefficient of the coatings on the process parameters. Special attention is paid to the study of the influence of the films nonstoichiometry on absorption in the visible and near-infrared ranges of the spectrum. The results allow concluding that the dominant mechanism responsible for absorption in titanium dioxide films in the near-infrared range of the spectrum is the deviation from the stoichiometric composition. This deviation is caused by the presence of defects in the coating structure such as oxygen vacancies (ions Ti^{3+}), which are seen as electron traps. As oxygen pressure and ionic current increase, the absorption of titanium dioxide films is reduced, and films with a composition closer to stoichiometric are obtained. In turn, the absorption of titanium dioxide in the visible spectrum (at wavelengths of 532 nm and 670 nm) has less to do with defects in stoichiometry, in contrast to contaminating impurities contained in the starting material, in the vacuum chamber and in the jet gas.

Keywords: *titanium dioxide, reactive thermal evaporation, activated reactive thermal evaporation, electron beam evaporation, absorption, stoichiometry, photothermal radiometry.*

Introduction

Films of titanium dioxide TiO_2 are extensively used for obtaining various types of interferential coatings in optical instrument making and quantum electronics [1–3]. Coatings based on TiO_2 show high mechanical strength, chemical durability and increased adhesion to the substrate. The most widespread and simple method for applying thin-film coatings of titanium dioxide is reactive thermal evaporation (RTE). However, the optical quality of coatings obtained by this method is considerably lower than the quality of titanium dioxide coatings obtained by means of other methods: for example, electron beam physical vapor deposition (EBPVD), ion beam target sputtering or magnetron sputtering. The listed methods based on target material sputtering by ions allow to obtain films with a polycrystalline structure having higher stability and lower optical losses. However, these methods are less productive, more difficult and economically more expensive than RTE.

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It is known [1] that the efficiency of evaporated substances deposition considerably increases with increasing reactivity of vapor particles. One of possible ways of increasing reactivity is as follows. The ions of one of the interacting components (oxygen) are created by means of a glow discharge, through which the particles of other components (molecules of the starting material of a coating, for example, TiO) pass. This method is called activated reactive thermal evaporation (ARTE) [4–6]. Using this method it is possible to obtain thin-film coatings of titanium dioxide, the optical losses of which are close to those of films obtained by means of EBPVD or ionic sputtering, especially in the near IR region.

It should be emphasized that the literature on obtaining high-quality optical films based on titanium dioxide does not provide systematized comparative data on the absorption in thin-film coatings in the visible and near infrared region and on factors affecting it. In our opinion, a comparative study on the spectral dependence of the absorption of thin-film coatings of titanium dioxide obtained by means of RTE and ARTE will allow to establish factors determining the mechanism of absorption in titanium dioxide coatings.

Thus, the purpose of this work was to compare the values of optical absorption in titanium dioxide coatings obtained by RTE and ARTE, and also to detect its dependence on the technological process parameters. Special attention is paid to the establishment of the influence of the non-stoichiometric composition of the films on absorption in the visible and near IR region. Because absorption in TiO_2 films substantially determines the laser durability of multilayer coatings based on them [7], the relevance of this work is undoubted.

Experimental

The studied films of titanium dioxide were deposited on flat polished substrates of fused quartz. Tablets of titanium monoxide TiO obtained by various methods were used a starting material for obtaining the films.

Absorption in the single-layer films of TiO_2 was measured at four wavelengths (1340, 1064, 670 and 532 nm). In order to exclude the influence of electric field distribution in the films on the measurement results, coatings of the same optical thickness for each of the above wavelengths were applied on glass substrates (optical thickness $\lambda/4$).

A laser based on yttrium orthoaluminate with neodymium ($YAlO_3:Nd^{3+}$) and a laser based on yttrium aluminum garnet with neodymium ($YAG:Nd^{3+}$) with wavelengths 1340 and 1064 nm, respectively, were used as radiation sources. The lasers operated in the mode of optical-acoustic Q-modulation. In all the cases the frequency of impulses repetition was 10 kHz. The average power of radiation at the main wavelength was ~ 60 W. Radiation with wavelengths

670 and 532 nm was obtained by intracavity transformation into the second harmonic of the main radiation of the $YAlO_3:Nd^{3+}$and $YAG:Nd^{3+}$ lasers. The average radiation power of the second harmonic was ~ 5 W. The main radiation frequency was transformed into the second harmonic by placing a standard crystal of $KTiOPO_4$ (KTP) in the resonators of the lasers. In all cases the lasers operated in the mode of one transverse TEM_{00} mode. No special actions were taken to optimize the coefficient of transformation into the second harmonic in order to increase the coefficient.

Losses due to absorption in the studied coatings were measured by means of laser photothermal radiometry [8–11].

To increase the efficiency of collecting thermal radiation we applied a two off-axis parabolic mirrors on the reception platform of the photodetector (a cooled single-element IR photodetector based on a three-component CdHgTe solid solution) as in [12] (see Figure 1). Calibration of the registered photothermal signal in units of the absorption coefficient was made according to the technique described in [11].

Results and Discussion

The method of laser photothermal radiometry (LPTR) [8–11], by means of which losses due to absorption in the studied coatings were measured, is an alternative to the conventional methods of absorption spectroscopy when measuring low absorption. A fundamental difference between LPTR and passive radiometry is that in case of LPTR the temperature derivative of thermal radiation flow is registered instead of the value of flow itself. The essence of the method consists in the following. In the course of measurements the studied sample is affected by periodical impulses of laser radiation. Owing to partial absorption of laser radiation and heat evolution, modulation of the surface temperature and of the registered thermal signal at the frequency of the laser impulses repetition takes place. The registered signal of thermal radiation depends on the quasiperiodic fluctuation of temperature, which is linear in absorption size. The method has a significantly higher sensitivity than the spectrophotometric methods based on the measurement of transmittance, because it uses the direct measurement of absorbed heat, and not the measurement of small changes of the signal against the background of a large value. Thus, it is noted in [11] that LPTR allows measuring ~ 0.001% and smaller losses due to absorption in coatings.

The scheme of the experimental unit for measuring low absorption in optical coatings by means of LPTR is shown in Figure 1.

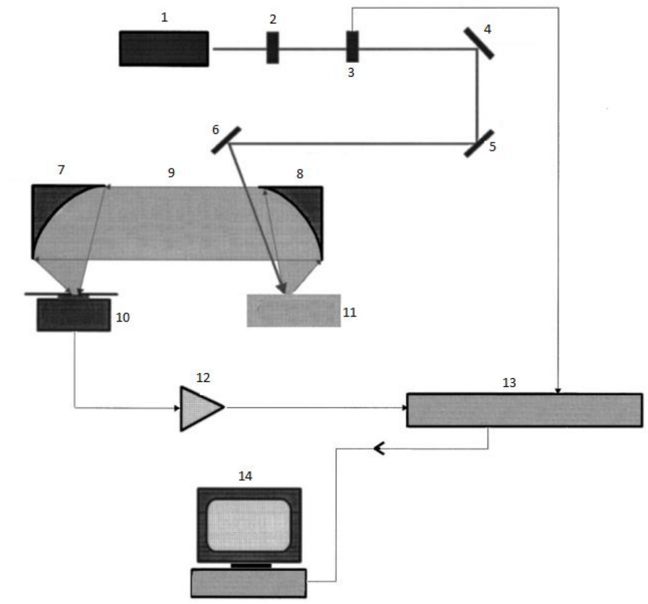

Figure 1. The scheme of an installation for measuring low absorption in coatings by LPTR:
1 – laser; 2 – polarizer; 3 – optical-acoustic modulator; 4, 5, 6 – hinged mirrors; 7, 8 – off-axis parabolic mirrors; 9 – thermal radiation; 10 – HgCdTe photodetector; 11 – sample; 12 – preamplifier; 13 – synchronous detector; 14 – computer) [12].

In this work dependences of absorption coefficients on the partial pressure of oxygen p_{O_2}, on ionic current density j when working with ionized oxygen, on film deposition rate v and on substrate temperature T were studied. Figure 2 shows dependences of absorption coefficient α on ionic current density j.

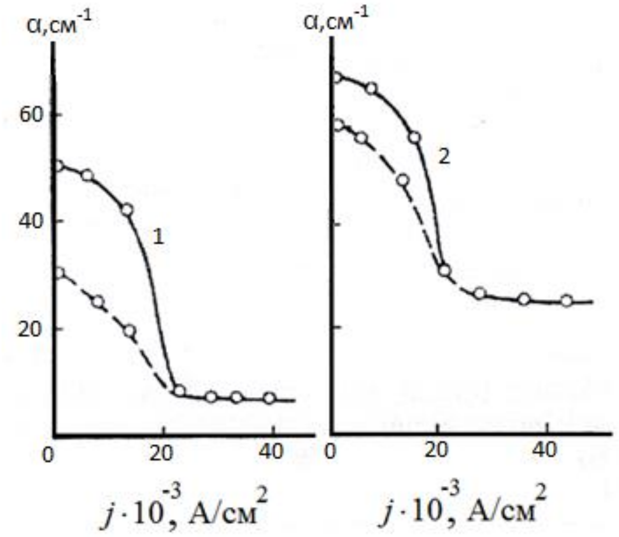

Figure 2. Dependence of absorption coefficient α in TiO_2 films measured at wavelengths of radiation 1064 (1) and 532 (2) nm on ionic current density j (the unbroken curve: $p_{O_2} = 1.5 \cdot 10^{-4}$ Mbar; the dashed curve: $p_{O_2} = 3.0 \cdot 10^{-4}$ Mbar; substrate temperature $T = 200°C$; film deposition rate $v = 0.45$ nm/sec^2).
[см$^{-1}$ means cm^{-1}; А means A; см^2 means cm^2]

Ionic current was measured by placing a special probe in the flow of ionized oxygen. In the course of sputtering the distance from the evaporator to the probe was equal to the distance from the evaporator to the substrates. It can be seen from the curves given in Figure 2 that the dependence of $\alpha(j)$ is more pronounced for absorption measured at 1064 nm than in the visible range. As current density j increases, the expected decrease in absorption coefficient α is observed at all wavelengths. The value of α is stabilized starting with j = 25.0 mA/cm^2, and further growth of current density does not result in its noticeable decrease, other parameters being invariable.

The obtained result allows concluding that when current density exceeds the value j = 25.0 mA/cm^2, the maximum level of titanium dioxide films oxidation is attained, at which the minimum values of absorption in the near IR and in the visible range significantly differ from each other. This can be only if the main mechanisms of absorption in these spectral intervals are various. Note also the fact that the pressure of oxygen has a considerably greater influence on absorption in the near IR than in the visible range. This also confirms the stated point of view.

Besides, it follows from Figure 2 that absorption coefficient $\alpha(\lambda)$ just slightly depends on p_{O_2} when working with ionized oxygen at j > (20.0–25.0) mA/cm^2. The main experimental results were obtained at p_{O_2} = (1.5–2.0)·10^{-4} mbar, because films having rather high refraction indexes (2.35–2.45) are obtained in this pressure range.

Figure 3 presents dependences of the absorption coefficient on the rate of films deposition.

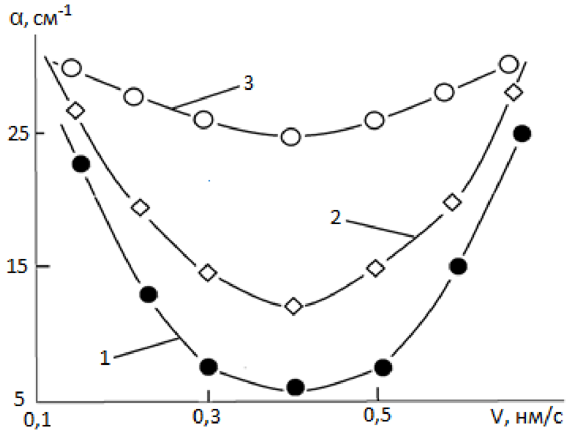

Figure 3. Dependence of the absorption coefficient of TiO_2 films at wavelengths 1064 (1), 670 (2) and 532 (3) nm on the rate v of films deposition:
p_{O_2} = 1.5·10^{-4} mbar, j = 25.0 mA/cm^2, T = 200°C.
[см$^{-1}$ means cm^{-1}; нм/с means nm/s]

One can see that the presented curves have a rather pronounced minimum corresponding to deposition rate about 0.45 nm/s, at which the smallest value of absorption coefficient is attained. The obtained dependences can be explained by taking into account the fact that the rate of titanium monoxide oxidation decreases as the film growth rate increases. At the same time, when the rate of the starting material deposition is small, oxygen molecules have time to desorb from the substrate surface before they enter the oxidation reaction with the initial molecules of the deposited material.

It should be emphasized that the dip of the curves becomes less pronounced as the wavelength decreases, and this unambiguously counts in favor of the assumption that the film composition stoichiometry affects the absorption coefficient at different wavelengths. Most likely, the deviation of a film composition from stoichiometric makes a prevailing contribution to the absorption coefficient in the near IR range. As for the visible range, the main contribution to absorption is caused by foreign substances and impurities of variable valency contained in the starting material, for example, by Cr^{3+} and Fe^{3+}. Besides, impurities can be due to contaminants existing in the chamber or introduced upon the reactive gas supply.

It follows from the dependences of the absorption coefficient on the substrate temperature given in Figure 4 that when the ionic current density is relatively low, absorption coefficient α in the films considerably increases as temperature grows. As *j* increases, the dependence becomes weaker, and starting with j = 25.0 mA/cm^2 absorption coefficient α practically does not depend on temperature as its changes from ambient to 350°C.

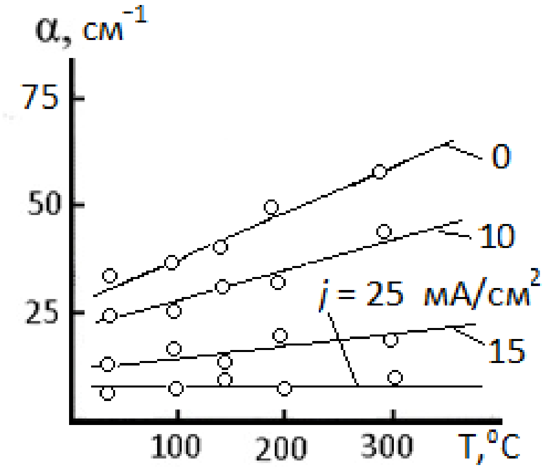

Figure 4. Dependence of the absorption coefficient of TiO_2 films (λ = 1064 nm) on the substrate temperature at different values of ionic current density: $p_{O_2} = 1.5\cdot10^{-4}$ mbar, v = 0. 45 nm/s^2. [см$^{-1}$ means cm^{-1}]

As we can see, when oxygen reactivity is high (j = 25 mA/cm^2), the minimum absorption coefficient is attained even at rather low substrate temperatures, the composition of the titanium dioxide films being closest to stoichiometric. When oxygen reactivity is low, the absorption coefficient grows as the substrate temperature increases. In our opinion, the growth of the absorption coefficient of the films is caused by an increase in the rate of oxygen molecules desorption with increasing substrate temperature.

Spectral dependences of the average absorption coefficient of the titanium dioxide films obtained by the RTE method in the presence of neutral or ionized oxygen in the chamber are given in Figure 5.

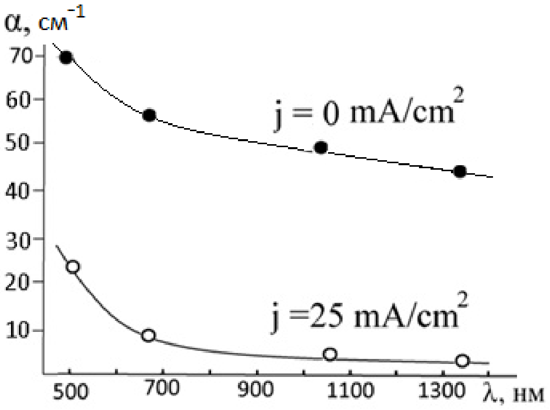

Figure 5. Spectral dependence of the absorption coefficient in TiO_2 films at p_{O_2} = $1.5 \cdot 10^{-4}$ mbar, v = 0.45 nm/c^2 and T = 200°C.
[см$^{-1}$ means cm^{-1}; нм/с means nm/s]

The table lists the values of absorption A and absorption coefficient α measured at the considered wavelengths. In case of small losses due to absorption ($A \ll 1$) these values are connected with each other by a simple equation:

$A = \alpha \cdot d = \alpha \cdot \lambda / 4n$,

where d is the film thickness, and n is the refraction index.

The measured values of the refraction index of the films are as follows: $n_{(\lambda\,=\,532\text{ nm})} = 2.35$; $n_{(\lambda\,=\,670\text{ nm})} = 2.33$; $n_{(\lambda\,=\,1064\text{ nm})} = n_{(\lambda\,=\,1340\text{ nm})} = 2.30$.

Parameters of TiO_2 films absorption

Starting material	Sputtering method	p_{O_2}, 10^{-4} mbar	Oxygen ionization	λ = 1340 nm		λ = 1064 nm		λ = 670 nm		λ = 532 nm	
				A, %	α, cm^{-1}	A, %	α, cm^{-1}	A, %	α, cm^{-1}	A, %	α, cm^{-1}
TiO	RTE	3	No	0.025	28.1	0.024	30.0	0.015	18.0	0.048	60.0
TiO	RTE	1.5	No	0.040	45.0	0.040	48.0	0.05	62.0	0.055	69.0
TiO	RTE	1.5	Yes	0.005	5.5	0.005	6.0	0.008	10.0	0.020	25.0
TiO_2	EBPVD	1.5	No	0.004	5.0	0.004	5.6	0.007	9.2	0.018	22.0

It can be seen from the table (the third line) that the use of ionized oxygen in the chamber upon sputtering films by the method of reactive thermal evaporation significantly reduces the absorption coefficient in TiO_2 films making it close to the value typical of electron beam sputtering (the last line of the table). Note that the relative measurement error does not exceed ±10%, and the confidence coefficient is 95%.

It is essential that titanium dioxide films with low values of the absorption coefficient can be obtained with the use of simpler and more readily available equipment. The value of ionic current density is an additional parameter allowing to affect purposefully the optical characteristics of coatings.

Conclusions

The results of the work allow concluding that the dominating factor responsible for the absorption of titanium dioxide films in the near IR range of the spectrum is the deviation of their composition from stoichiometric, i.e., the existence of defects in the form of oxygen vacancies (Ti^{3+} ions) in the films structure. They are considered as electronic traps [13, 14]. This conclusion is confirmed by the fact that increasing parameters p_{O_2} and j decreases absorption in the titanium dioxide films, that is, films with a composition closer to stoichiometric are obtained. The obtained result confirms the assumption stated in [15, 16] that the non-stoichiometric composition of TiO_2 films affects the value of radiation absorption in them.

In turn, the absorption of titanium dioxide in the visible range of the spectrum (at wavelengths 532 and 670 nm) is due to impurities (apparently, Fe^{3+}, Cr^{3+} and other transition elements ions) contained in the starting material, in the vacuum chamber and in the inlet gas rather than due to stoichiometry defects.

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