Magnetron sputtering system with reactive plasma assisting for deposition of Ti$_x$Zr$_{1-x}$O$_2$ coating resistant to laser radiation

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Abstract. The magnetron sputtering system with reactive oxygen plasma assisting for deposition of Ti$_x$Zr$_{1-x}$O$_2$ nanocomposite coatings by sputtering a single Ti-Zr target and the results of study of the stability of these coatings to the action of high-power laser radiation are presented. The periodically repeated sequential processes of applying sputtered material onto a substrate and oxidation of the deposited material have been realized for obtaining the optical coating with resistance to the 960 W/cm$^2$ laser radiation.

1. Introduction
Titanium and zirconium oxides are highly refractive optical materials that are weakly absorbing in the visible and near infrared ranges. These materials are characterized by high thermal, chemical, mechanical and dielectric stability; they find application in optical devices requiring the resistance of elements to laser radiation. At present, mixtures of Ti and Zr oxides are of particular interest as promising materials for optical technology [1–3]. Using the mixtures allows you to get a new set of their properties.

However, the implementation of high resistance to laser radiation requires certain technological approaches. So, for ZrO$_2$ at a high level of heat exposure, structural transitions from one modification to another are characteristic. For structural stabilization of ZrO$_2$, it is doped, for example, with yttrium oxide. Both Ti and Zr, in compounds with oxygen, can have different degrees of oxidation, which leads to stoichiometric deviations and deterioration in their laser resistance. In this regard, it is necessary to study the resistance to the action of laser studies of coatings from different mixtures of these oxides in order to establish the possibility of their use as persistent highly refractive layers of dielectric mirrors. We are not aware of published data on the laser strength of coatings of the composition Ti$_x$Zr$_{1-x}$O$_2$.

Currently, a popular method of applying oxide optical coatings is ion sputtering in a magnetron system (MS). To implement this method, various MSs are used with additional activation of the reactive gas to assist the process of synthesis of desired oxides on substrates [4–7]. The purpose of this work is the creation of a magnetron ion-sputtering setup with reactive plasma assisting for deposition
of Ti$_x$Zr$_{1-x}$O$_2$ nanocomposite coatings by sputtering a single Ti-Zr target; the other aim is study of the stability of these coatings to the action of high-power laser radiation.

2. Experimental setup and procedure
The scheme of experimental setup for coating deposition is shown in figure 1. The magnetron system MS for ion sputtering of the target T from source material and plasma generator for activation of reactive gas (oxygen in our case), using the gas discharge system GDS, are built in the form of autonomous spatially separated blocks with separate gas supply. The flat design of the substrate holder of a carousel type and small gaps between it and the upper ends of those blocks provide fairly independent gas environments in them under the condition of dynamic equilibrium between the gas inlet velocity and the pumping-out speed.

![Figure 1. Installation scheme: RF – radio-frequency power inputs, OP – oxygen plasma, T – target (MS cathode), S – substrates, GDS – gas discharge system of the plasma generator.](image)

The design of our technological installation implements the substrates rotation and the periodically repeated sequential processes of “applying sputtered material onto a substrate” and “oxidation of the deposited material” in contrast to the installation [7] with parallel processes of “applying” – “oxidation”. The radio-frequency (RF) power supply of MS and GDS at frequency of 13.56 MHz with power of 300 W of each ensured high sputtering rates of the metal Ti-Zr target T and efficient oxidation of the oxide layers growing on substrates S. At the given power of MS, taking into account the area of the sputtering zone of the target T, the specific power of the RF magnetron discharge was about 10 W/cm$^2$. The fast alternating nature of the RF voltage on the target T, serving as MS cathode, and on the gas discharge system GDS guaranteed the absence of arcing on the electrodes and substrates. For the manufacture of targets, alloys of the Ti$_x$Zr$_{1-x}$ composition were used, where x was 1, 0.6, 0.5, 0.4, 0.3 and 0. The diameter of the target was 76 mm, the distance from the target T to the carousel was 50 mm. The deposition processes were carried out without external heating K8 and BK7 glass substrates with a total pressure in the working chamber of about 3 mTorr. The carousel rotational speed was 150 min$^{-1}$. Optical measurements were carried out with СФ-2000 spectrophotometer. The method of measuring the coating refraction index $n$ is presented in [8]. The laser strength of the layers was evaluated according to the procedure [9] in accordance with OST 11 070.802-80, OST 3-5626-83, ISO 11254-1. Single-mode pulsed laser radiation at the wavelength of 1064 nm was used; the beam diameter was 0.26 mm; the number of pulses with the duration $(10 \pm 2)$ ns of radiation acting in one point on a sample was not less than 100.

3. Results and discussion
The dependence of the refraction index of the coatings on the composition of the sputtered targets at the wavelength of 550 nm is shown in figure 2. Coatings with the thickness of 300 nm were deposited when Ar was supplied to the MS and O$_2$ was supplied to the GDS of the oxygen plasma generator, respectively. In this case, the oxygen concentration in the space above the target T did not exceed 10 % that minimized the oxidation of the target surface. Accordingly, the coating growth rate on the rotating substrates was about 0.25 nm/s. Note, with increase of the oxygen content in the space above target T from 10 % to 20 %, the coating growth rate dropped sharply due to more intense oxidation of targets. As it can be seen from figure 2, the dependence of the coating refraction index $n$ on the target composition is not linear in general. However the coatings obtained with the targets with Ti content
≥ 40 %, the dependence of the refraction index \( n \) on the concentration of Ti in the target is observed as close to linear one. Herein, when the Ti content in the target corresponds to pure titanium we see the maximal value of index \( n \), which is characteristic of the pure TiO\(_2\) coating. We connect this with the nucleation and growth of the crystalline phase of TiO\(_2\) tetragonal modification. Indeed, preliminary electron microscopic studies showed that the ZrO\(_2\) layers obtained under the indicated conditions are characterized by a largely amorphous structure with a small fraction of finely crystalline inclusions. The TiO\(_2\) layers are characterized by a predominance of the crystalline phase of the tetragonal modification with crystallite sizes up to 12 nm with a small fraction of the amorphous phase.

![Figure 2](image-url)

**Figure 2.** Dependence of the coatings refractive index on the Ti content in the target material.

When the Ti content \( x \leq 30 \% \) the index \( x \) is actually equal to that for ZrO\(_2\). It could be assumed that TiO\(_2\) dissolves in ZrO\(_2\) with a quantitative dominance of the latter. However, the state diagram indicates the extremely low solubility of TiO\(_2\) in ZrO\(_2\). Thus, Ti atoms are likely to be in a state, which is not characteristic of its basic oxide.

Figure 3 shows the laser strength of the coatings at different concentrations of Ti and Zr in the target materials.

![Figure 3](image-url)

**Figure 3.** Laser strength of the coatings obtained at different values of Ti content in the target material.
One can see from figure 3, the threshold values of the coating laser damage strongly dependent on the concentration of Ti in the target material and, as a consequence, on the coating composition. The maximal values of the strength to laser radiation correspond to $x = 40\text{-}50\%$ that is at approximately equal concentrations of Ti and Zr in the deposited coatings. Microscopic analysis of the damage type of zones on the coating surface showed that it was characteristic for that of the dielectric breakdown mechanism. This indicates that the deposited oxide coatings present a purely dielectric material.

4. Conclusions
As it can be seen, the presented technological approach provides obtaining the high resistance of the highly refractive Ti$_x$Zr$_{1-x}$O$_2$ coatings to laser radiation (up to 960 MW/cm$^2$), This is sufficient for the application of the obtained coating in various power lasers and optical apparatus, including space photonic devices. The presence of the maximum in the data on figure 3 seems very interesting and requires further study.

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