Influence of oxygen fraction on the characteristics of titanium oxide coatings obtained by the magnetron method

V S Vashchilin1, E V Krivinozhk1, L S Sabitov2,3, S V Trukhanov5 and L KH-A Saipova6

1Belgorod State Technological University named after V G Shukhov, Kostyukov St, 46, Belgorod, 308012, Russia,
2Federal State Autonomous Educational Institution of Higher Education «Kazan Federal University», Kremlyovskaya St, 18, Kazan, 420008, Russia
3Kazan State Power Engineering University, Krasnoselskaya St, 51, Kazan, 420066, Russia
4Federal State Autonomous Educational Institution of Higher Education «Kazan Federal University», Kremlyovskaya St, 18, Kazan, 420008, Russia
5Federal state budget educational institution of higher education «MOSCOW STATE UNIVERSITY OF CIVIL ENGINEERING (NATIONAL RESEARCH UNIVERSITY)"
6Grozny State Oil Technical University named after academician M.D. Millionshchicov

E-mail: vvs25@yandex.ru

Abstract. Titanium oxide coatings were obtained by magnetron sputtering on a glass substrate with different oxygen fraction in the plasma. Studies were carried out by scanning electron microscopy of the obtained coating samples establishing the role of oxygen in the process of crystallization of TiOx-coatings. It was found that with increasing the oxygen fraction in the vacuum arc discharge plasma the crystal grain size increases, the time of coating on the substrate increases, and the crystal layer has a columnar structure. The presence of amorphous and crystalline phase for all coating samples was revealed, with the predominance of the former. On the surface microphotographs of the coatings microcraters were found, on the surface of the samples obtained at the concentration of O2 in the plasma 14% of their concentration is maximum, this can be explained by changes in the state of the plasma, starting to occur at this concentration of reaction gas. Vacuum photonic annealing of the obtained coatings was performed. Vacuum radiation annealing in the furnace led to modification of coatings: sintering of coatings, increase of their crystallinity. An increase in crystallite size in a sample with an oxygen fraction of 12% was detected.

1. Introduction
Titanium oxide coatings are used in optical instrumentation because of their high refractive index (n = 2.6-2.9), which in combination with increased hardness and chemical resistance make this coating in demand in industry [1]. TiOx coatings are included in the compositions of light-correcting layers on window glasses, hardening coatings on glass containers [2] and are the basis of self-cleaning coatings [1] on various products. In addition, titanium dioxide coatings on implants promote their fusion with
living bone tissue [3]. Microelectronics is also showing interest in thin-film titanium oxide as a chemosensor system [4] and as a promising material for information storage devices [5].

In the industry for the use of titanium oxide coatings, their structural-phase state plays a huge role, which depends on the deposition method and process parameters. Among the numerous methods of deposition of TiO$_x$ coatings [6], the reactive magnetron sputtering method stands out, the advantages of which are: 1) the ability to obtain dense coatings, 2) the possibility of obtaining a coating of equal thickness on a large area of application, 3) the ability to vary the structure and phase composition of the coating without significantly changing the sputtering speed and substrate heating. At the same time, most papers, e.g., [7-12], linking the technological parameters of magnetron deposition with the phase composition of TiO$_x$ coatings, do not indicate the role of oxygen in the coating crystallization process. One can note the articles [13] and [14], which found the appearance of maximum crystallinity of coatings at certain fractions of O$_2$ in the plasma. However, the reasons for this phenomenon are not indicated by the authors [15].

2. Materials and methods
The substrates on which the TiO$_x$ coatings were deposited were “MiniMed” slides with dimensions of 76x25x1 mm. The substrates were cleaned by soaking in a concentrated chromium solution for 4 days before coating. After that, the potential substrate was cleaned twice in distilled water from the chromium mixture itself. The remainder of the distilled water was removed from the surface by a stream of compressed air. Just before the coating, the substrates were cleaned in a vacuum from trace amounts of organic impurities by argon ion bombardment for 15 min on the UniCoat 200 unit (discharge voltage 2100 V, discharge current 150 mA, pressure 0.09 Pa, argon flux 26 - 29 sccm).

Before each sputtering, the targets were additionally cleaned from the possible formation of a TiO$_x$ oxide film on their surface, the duration of which was 3 min for each load. Such actions were performed due to the fact that the sputtering of Ti atoms from the surface of a titanium target not covered by an oxide film is much easier than for a target with an oxidized surface, which cannot but affect the purity of the experiment (the sputtering ratio of Ti atoms from the surface of an unoxidized target is 0.3, with an oxidized target - 0.06).

Magnetron deposition of coatings was performed in the UniCoat 200 unit with a dual magnetron system and pulse power supply. Two titanium plates of BT1-00 grade with dimensions 198x78x6 mm each were used as targets [15]. Argon (Ar) was the working gas, and oxygen (O$_2$) was the reaction gas. The operating pressure was 0.17 Pa, the nominal discharge voltage was 580 V. The magnetrons were fed by bipolar pulses of 50 μs (20 kHz) duration in the mode of holding the discharge current at 4 A for each magnetron. The strength of the current supplied to the magnetrons in the process of sputtering was calculated with the prospect of reducing the time spent on sputtering of coating of a certain thickness.

The heat treatment was performed in the SemiTEq STE RTP150 fast temperature treatment unit. The process parameters were as follows: vacuum rarefraction p = 350 Pa; annealing temperature $\tau_{\text{ann}}$ = 350 °C; annealing time $\tau_{\text{ann}}$ = 5 min; maximum temperature rise time $\tau_{\text{max}}$ = 90 s; temperature rise rate $\nu_{\text{rise}}$ = 30 %. Annealing was performed using 36 lamps built into the furnace with a power of 2 W each; the utilization factor $K_{\text{util}}$ = 20%. Drying of the atmosphere inside the annealing chamber was performed with dry nitrogen (N$_2$) to the required humidity values. The humidity was determined by the dew point, the value of which was $t_{\text{dew}}$ = - 43 °C.

All data, including microphotographs and coating thicknesses/layers, presented in this paper were obtained using a MIRA3 TESCAN scanning electron microscope.

3. Results and discussions
Table 1 shows the thickness data for coating samples obtained at 10% and 12% of O$_2$ in plasma, and individual layers for the coating obtained at 14% of O$_2$ in plasma.
Table 1. Thickness of coatings as a function of oxygen fraction and vacuum annealing.

| Heat treatment, °C | Names of samples |
|-------------------|------------------|
|                   | 10 %  | 12 %  | 14 % (amorph.) | 14 % (cryst.) |
| Coating/layer thickness, nm | 350 | 500–510 | 460 | 250 | 150 |

In Figure 1 (a), on the right side, one can clearly see the boundary between the substrate (glass plate) and the TiO<sub>x</sub> coating, making it quite easy to understand that the coating consists of two expressed layers: amorphous (lower) and crystalline (upper) [16]. The crystalline layer has a columnar structure. In Fig. 1 (b, c) we can see that the surface of the coating is rather fine-grained, and the average grain size is ≈35 nm with a distribution range of 30-55 nm.

![Microphotographs of the chip (a) and surface (b, c) of the TiO<sub>x</sub> coating obtained in the magnetron deposition process at O<sub>2</sub> fraction in the plasma of 10%.](image1)

In Fig. 2 (a, b) we can see that TiO<sub>x</sub> coating obtained at 12 % of O<sub>2</sub> in plasma also has a crystalline structure only in its upper part (going to the surface), and in its lower part (contacting the substrate) is an amorphous structure with rare crystal impregnations, making some kind of a dense crystalline contact layer [15].

![Microphotographs of the chip (a, b) and surface (c, d) of the TiO<sub>x</sub> coating obtained during magnetron deposition at O<sub>2</sub> fraction of 12% in plasma.](image2)

It can also be seen from Fig. 2(a) that this coating can also contain relatively large microcrystals that grow to the full thickness of the coating, but this phenomenon should rather be considered an exception. When comparing the right part of the micrograph shown in Fig. 2 (b) with the right part of the micrograph in Fig. 1 (a), one can notice that the formed columnar microcrystal structure for the coating obtained at 10% of O<sub>2</sub> in plasma takes a larger share in the coating than for the coating obtained at 12% of O<sub>2</sub> in plasma.
Figure 3. Microphotographs of the chip (a, b) and surface (c-e) of the TiO_x coating obtained during magnetron deposition at O2 fraction of 14% in plasma.

In Fig. 2 (c, d) we can see that the examined coating, just as in the previous case, has a fine-grained morphology with an average grain size of ≈ 35 nm and a distribution range of 30-50 nm.

In Fig. 3 (a, b) we can clearly distinguish 2 clearly distinguishable layers: the thicker lower layer (amorphous) and the thinner upper layer (crystalline). When comparing these microphotographs with the microphotographs presented in Fig. 1 (a) and 2 (a, b), we can see that the crystal layer of the coating obtained at 14 % of O_2 in plasma is well oriented along the axis perpendicular to the surface and has a relatively loose structure, whereas the two previous samples examined are more characterized by a dense crystal layer structure.

Fig. 3 (c, d) shows that the considered coating has a coarser grain structure (average grain size ≈ 42 nm; distribution range = 35-60 nm) than in the two previous cases considered, and the coating surface is largely textured. Moreover, crystals of larger size are located higher in the level of relatively smaller crystals, thus forming a network of elevations with troughs.

In addition to all of the above, we can also pay attention to the fact that all the samples without exception have formations resembling craters, i.e., they have a shape close to a circle, the edges of which are higher in level relative to the surrounding microrelief, and the conventional center is lower or at the same level with the surrounding microrelief. Such forms of microrelief could be formed as a result of destruction under the influence of plasma ions of another form of microrelief - the outgrowths, and, most likely, having a hollow core. Nevertheless, with decreasing the surface imaging scale for samples “10%” and “12%”, these microcraters are no longer displayed, and on microphotographs with a larger imaging scale, these formations become visible only at high contrast levels of microphotographs (Fig. 1, c; 2, d), which can indicate, in general, the smaller size of these microcraters (ø ≈ 1-1.5 µm) and their presence in much smaller quantities compared to the “14 %” samples (Fig. 3, d). In addition, when zooming out, a group of microcraters (ø = up to 1.3 µm) uniformly located at approximately equal distances from each other (d ≈ 4.2-6.5 µm) becomes visible in the microphotograph of the “14 %” sample (Fig. 3, e).
The increase in the concentration of microcraters on the surface of samples obtained at \( \text{O}_2 \) concentration of 14% in plasma can be explained by changes in the plasma state that begin to occur at this concentration of reaction gas.

Fig. 4 (a) shows that after heat treatment, the coating applied to the glass substrate acquired a densely heterogeneous structure consisting of fairly large crystals in height. There was no amorphous phase. Fig. 4 (b, c) shows that the coating surface is a fine-grained structure and differs little from the surface of the same coating before heat treatment. The only exception is the appearance of rather sparsely located and, in addition, small in size neoplasms, which look like “knots” and represent aggregates of microcrystals located higher in level relative to the general level of coating microcrystals (Fig. 4, c).

Figure 4. Microphotographs of the chip (a) and surface (b, c) of the TiO\(_x\) coating obtained during magnetron deposition at the \( \text{O}_2 \) fraction of 10% in the plasma, after heat treatment.

Figure 5 (a) shows that the coating acquired a dense, coarse-crystalline structure after heat treatment. In Fig. 5 (b) we can also understand that the surface of the coating obtained after annealing, in general, did not change in terms of grain size of microcrystals, also similar to the previous case. Significant changes can be found in Fig. 5 (c), from which we can see that the coating is abundantly dotted with “knots” of microcrystal aggregates located above the general level of the coating surface, which can be seen especially clearly in Fig. 4.9 (a). According to Fig. 4 (c), 5 (c) we can trace a certain analogy of changes occurring during heat treatment of “10%” and “12%” coatings, with the significant difference that for “12%” coating the aggregates are formed in much greater number per unit area (25 pcs/25 \( \mu \text{m}^2 \) against 9 pcs/25 \( \mu \text{m}^2 \)) and have much greater dimensions (\( \omega = 0.3 \mu \text{m} \) versus \( l = 0.2 \mu \text{m} \)).

Figure 5. Microphotographs of the chip (a) and surface (b, c) of the TiO\(_x\) coating obtained during magnetron deposition at the \( \text{O}_2 \) fraction of 12% in the plasma, after heat treatment.
Fig. 6 (a) shows that the structure of the upper (crystalline) coating layer after the heat treatment practically did not undergo changes, but in the lower (amorphous) layer during the annealing process, its crystallization occurred.

![Microphotographs of the chip and surface of the TiO\textsubscript{2} coating obtained during magnetron deposition at the O\textsubscript{2} fraction of 14 % in the plasma, after heat treatment.](image)

According to the microphotographs in Fig. 6 (b, c) we can conclude that no significant changes in the surface structure of the “14 %” coating occurred during heat treatment [17].

4. Summary
It was found that with increasing the oxygen fraction in the vacuum arc discharge plasma the crystal grain size increases, the time of coating on the substrate increases, and the crystal layer has a columnar structure. The presence of amorphous and crystalline phase for all coating samples was revealed, with the predominance of the former. On the surface microphotographs of the coatings microcraters were found, on the surface of the samples obtained at a concentration of O\textsubscript{2} of 14% in plasma their concentration is maximum, this can be explained by changes in the state of the plasma, starting to occur at this concentration of reaction gas. Vacuum radiation annealing in the furnace led to sintering of coatings increasing their crystallinity. An increase in the crystallite size in the sample with an oxygen fraction of 12% was detected.

5. References
[1] Diebold U 2003 The surface science of titanium dioxide Surface Science Reports 43 53-229
[2] Minko N I, V M Nartsev 2014 Strength and methods of glass hardening: monograph 2nd ed. Belgorod: Publishing House of BSTU named after V.G. Shukhov 152
[3] López-Huerta F, Cervantes B, González O 2014 Biocompatibility and surface properties of TiO\textsubscript{2} thin films deposited by DC magnetron sputtering Materials 7 4105-4117
[4] Yordanov R, Boyadjiev S, Georgieva V 2014 Characterization of rf and dc magnetron reactive sputtered TiO\textsubscript{2} thin films for gas sensors Digest Journal of Nanomaterials and Bionanomaterials 9(2) 467-474
[5] Kwak J S, Do Y H, Lee J H 2008 Resistive switching properties of a polycrystalline TiO\textsubscript{2} memory cell with a tungsten nitride (WN) buffer layer inserted Journal of the Korean Physical Society 53(6) 3685-3689
[6] Zhou W, Zhong X, Wu X 2006 Structural and optical properties of titanium oxide thin films deposited on unheated substrate at different total pressures by reactive dc magnetron sputtering with a substrate bias Journal of the Korean Physical Society 49(5) 2168-2175
[7] Mráz S, Schneider J M 2011 Structure evolution of magnetron sputtered TiO\textsubscript{2} thin films Journal of Applied Physics 109 id 023512. 6 p.
[8] Stamate M, Lazar G, Lazar I 2008 Anatase – rutile TiO\textsubscript{2} thin films deposited in a D.C. magnetron sputtering system Romanian Journal of Physics 53(1-2) 217-221
[9] Suhail M H, Mohan Rao G, Mohan S 1992 DC reactive magnetron sputtering of titanium - structural and optical characterization of TiO₂ films Journal of Applied Physics 71 1421-1427

[10] Boukrouh S, Bensaha R, Bourgeois S 2008 Reactive direct current magnetron sputtered TiO2 thin films with amorphous to crystalline structures Thin Solid Films 516 6353-6358

[11] Mukherjee S K, Nebati A, Mohtascham F 2014 Influence of thickness on the structural properties of radio-frequency and direct-current magnetron sputtered TiO₂ anatase thin films Thin Solid Films 558 443-448

[12] Zhang C, Ding W, Wang H 2009 Influences of working pressure on properties for TiO₂ films deposited by DC pulse magnetron sputtering // Journal of Environmental Sciences 21 741-744

[13] Baroch P, Musil J, Vlcek J 2005 Reactive magnetron sputtering of TiOₓ films Surface and Coatings Technology 193 107-111

[14] Zhao B, Zhou J, Rong L 2010 Microstructure and optical properties of TiO₂ thin films deposited at different oxygen flow rates Transactions of Nonferrous Metals Society of China 20 1429-1433

[15] Nartsev V M, Atkarskaya A B, Zaitsev S V, Vashchilin V S, Prokhorenkov D S 2015 Investigation of the effect of the oxygen fraction in plasma on the phase composition of TiOₓ coatings deposited by the magnetron method Refractories and technical ceramics 3 10-16

[16] Vashchilin V S, Krivonozhko E V 2020 Studies of the dependence of the influence of the O₂ fraction on TiOₓ coatings obtained by magnetron sputtering Actual directions of scientific research of the XXI century: theory and practice 8 (2) 40-46

[17] Zaitsev S V, Vashchilin V S, Prokhorenkov D S, Limarenko M V, Evtushenko E I 2018 Influence of Annealing Temperature on the Microstructure and Morphology of TiN Films Synthesized by Dual Magnetron Sputtering Technical Physics 63(8) 1189–1193

Acknowledgments
This work was realized in the framework of the Program «Priority 2030» on the base of the Belgorod State Technological University named after V G Shukhov. The work was realized using equipment of High Technology Center at BSTU named after V G Shukhov.