Structural features and nitrogen positions in titanium oxynitride films grown in plasma of magnetron discharge

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Abstract. The paper addresses the results of the analysis of the structural features of nitrogen-containing titanium oxides films, deposited by reactive magnetron sputtering. The films have a nanocrystalline two-phase structure and consist of anatase and rutile crystallites, regardless of the coating deposition regimes. No traces of titanium nitride phase are found in the film and nitrogen atoms in oxide form are localized at the grain boundaries of the deposited film.

1. Introduction

Recently, medical implantology has been developing towards the coating of implants with ultra-thin films. In particular, this refers to the formation of thin coatings based on binary and ternary compounds of titanium (oxides and oxynitrides), which have high bio- and hemocompatibility. This is especially true for stents used in vascular surgery [1–3].

Up to date, a number of works have studied the properties of titanium oxide and oxynitride films (TiON) deposited by ion-plasma methods [1–6] with reactive magnetron sputtering (RMS) having a special place among them.

Various impurity elements are used to modify the properties of TiO₂ films and nitrogen is very promising dopant. The purpose of this is to control the band gap of deposited titanium oxide films. The location of nitrogen atoms in the structure of TiO₂ film is of particular interest. Either nitrogen is localized in the regular or in interstitial position of the TiO₂ crystallite [7, 8]. The position of nitrogen atoms in N-TiO₂ films deposited by RMS technic remains unknown. Moreover, a number of works show the possibility that nitrogen is localized in the structure of the deposited coating in the form of oxides [6].

Thus, a nitrogen-containing titanium oxide films (N-TiO₂) formed with high-tech process contain two components: titanium oxide and nitric oxide (NO). The bioactivity of this type of coating is associated with the presence of oxide forms of nitrogen, and this is important for N-TiO₂ coatings for stents [9].
In this regard, the paper aims to study the structural features of nitrogen containing TiO$_2$ films (N-TiO$_2$) formed by the reactive magnetron sputtering and to determine the relationship between the microstructure features of the films and the conditions of their deposition.

2. Physicochemical characteristics and structure of N-TiO$_2$ magnetron deposited film

N-TiO$_2$ films have been deposited onto different substrates (stainless steel L316, silicon wafers, glass, KBr) using both planar and dual cylindrical magnetron in different deposition modes [3]. Titanium was the sputtered material and the working atmosphere consisted of argon, nitrogen, and oxygen in various ratio at a total pressure of (0.1–0.3) Pa. In several cases, a negative bias voltage $U_b = -100$ V was applied to the substrate and in the other modes the voltage was zero ($U_b = 0$).

Recent studies [4–6] show that N-TiO$_2$ films have a nanocrystalline two-phase structure and consist of anatase and rutile crystallites, regardless of the deposition mode and the nitrogen content in the reactive atmosphere. No trace of the titanium nitride phase was found in the film. The data of energy-dispersive analysis demonstrate the nitrogen concentration of (4–8) at% in the film. Analysis of TEM images showed that the films consist of nanoscale grains with distinct boundaries regardless of the deposition mode. The average crystallite size of TiO$_2$ film is about 20 nm and decreases to units of nanometers with nitrogen ratio increasing. The grain size distribution function is unimodal in all cases. The microdiffraction patterns demonstrated point reflexes belonging to the anatase and rutile phases. It should be noted that the data on crystallite sizes calculated using the TEM method are consistent with the results of the calculation of coherent scattering regions (CSR) from XRD patterns (table 1).

SEM and TEM data show that an increase in nitrogen content in the working atmosphere up to 70% leads to a decrease in the grain size (see table 1) in the coating, as well as to the formation of the quasi-homogeneous fine-grained structure of N-TiO$_2$ films deposited in the negative bias mode.

| $N_2/O_2$ ratio | Volume fraction, [%] | Mean CSR size, [nm] | Lattice parameters, [Å] | Relative deformation, $\Delta d/d$ |
|-----------------|----------------------|---------------------|-------------------------|-------------------------------|
|                 | anatase | rutile | anatase | rutile | anatase | rutile | anatase | rutile |
| $U_b = 0$       |          |        |          |        |          |        |          |        |
| 0 (TiO$_2$)     | 70   | 23    | 20      | 12     | a=3.793 | a=4.592 | c=9.549 | c=3.035 |
| 1 (N–TiO$_2$)   | 14   | 70    | 14      | 12     | a=3.795 | a=4.590 | c=9.538 | c=3.039 |
| 3 (N–TiO$_2$)   | 13   | 72    | 13      | 12     | a=3.798 | a=4.597 | c=9.598 | c=2.955 |
| $U_b = -100$ V  |          |        |          |        |          |        |          |        |
| 0 (TiO$_2$)     | 30   | 68    | 11      | 10     | a=3.793 | a=4.608 | c=9.551 | c=2.958 |
| 1 (N–TiO$_2$)   | 15   | 78    | 10      | 10     | a=3.781 | a=4.595 | c=9.495 | c=2.961 |
| 3 (N–TiO$_2$)   | 10   | 85    | 10      | 9      | a=3.768 | a=4.595 | c=9.531 | c=2.970 |

The coating structure is predominantly amorphous when argon is present in the working atmosphere and the discharge power density is more than 2.6x10$^3$ W·cm$^{-2}$, regardless of the presence of electrical bias. The microdiffraction pattern shows a diffuse halo in the presence of weak reflections from crystalline phases.

Anatase is the predominant phase in the TiO$_2$ film deposited in unbiased mode. The fraction of anatase decreases from 70% to 13%, and those of rutile rises from 23% to 72%, with the increase in N$_2$
ratio in the working gas from 0 to 70% (see table 1). Simultaneously, the size of coherent scattering regions (CSR) of the anatase phase decreases from 20 nm to 13 nm.

Unlike the unbiased mode, the predominant phase in the films obtained in the \( U_b = -100 \) V mode is rutile. Its share increases (from 68% to 85%) with increasing nitrogen content in the working gas, while the anatase content in the film is reduced to 10%, and the average CSR size is about 10 nm. Analysis of X-ray diffraction and TEM data shows that the nanoparticles in the film are anatase crystallites limited predominantly by the (101) and (100) planes, and rutile ones limited by the (110) planes. The investigation of the structural and phase characteristics of N-TiO\(_2\) films by Raman scattering and IR spectroscopy confirms the results of electron microscopic studies. Table 1 represents the calculated data on the phase composition and parameters of the crystallites comprising the film.

The chemical bonds in the deposited coatings were investigated by X-ray photoelectron spectroscopy (XPS). The analysis of high-resolution (HR) spectra indicates that titanium is oxidized to Ti\(^{4+}\) (TiO\(_2\) stoichiometry) regardless of the N\(_2\) ratio in the working gas [6].

The HR spectra of the oxygen level O1s contain peaks corresponding to Ti - O (529.9 eV), Ti - O - N (531.3 eV) and Ti - OH (532.4 eV) bonds, respectively. XPS spectra of HR of N1s nitrogen level displace the peaks referring to chemisorbed molecular nitrogen N\(_2\) (399.9 eV) and nitrogen oxides NO (402.0 eV) and NO\(_2\) (406.2 eV). Gibbs free energy of titanium nitride formation is \( \Delta G_{\text{TiN}} = -308.9 \) kJ/mol and \( \Delta G_{\text{TiO}_2} = -888.9 \) kJ/mol, and because of this difference TiN is not formed in the film structure. This implies the localization of oxide forms of nitrogen at intergranular boundaries of the film. A similar idea, first formulated in [6] explains the ultrafine film structure by localization of nitric oxide in form of two-dimensional layer on the planes limiting TiO\(_2\) nanocrystals during film growth. And such mechanism may describe the crystallite size reduction during their epitaxial growth in the plasma of magnetron discharge.

Nitrogen-containing N-TiO\(_2\) films deposited by the method of reactive magnetron sputtering possess high values of nanohardness (up to 26 GPa), Young's modulus (up to 231 GPa), elastic recovery (up to 70%) and high adhesion strength (up to 376 MPa) and these determine film good elastic properties and crack resistance.

Deposited coatings were investigated under conditions of long contact with biological fluids. The nitrogen-containing films were dissolved in physiological media, and then the composition of model liquids was studied with the methods of IR and raman spectroscopy, atomic emission analysis. In addition, gas chromatographic spectroscopy on a CHNS Flash 2000 Thermo Scientific elemental analyzer was used for analysis of films and solutions after keeping the film samples in them.

The following solutions were used as model liquids: Ringer's solution, urea, hydrochloric acid, acetic acid, lactic acid in appropriate concentrations of the body. The film was kept in Ringer's solution (6.5 g/l NaCl, 0.42 g/l KCl и 0.25 g/l CaCl\(_2\)) for 300 days.

Table 2 presents the CHNS analysis data, which demonstrate the presence of nitrogen in the amount of 8.731 weight% in the coating and 0.072 weight% in the solution. The latter indirectly indicates the presence of nitric oxide NO in model fluids. There is also hydrogen in the solution.

| Component | Exit time, min | Peak area, a.u. | Content, % |
|-----------|----------------|----------------|------------|
| N         | 0.983          | 26 015         | 8.731      |
| Solution  | 0.995          | 10 270         | 0.072      |
| N         | 4.758          | 6 373 734      | 10.320     |

In total, the data show a high chemical resistance of the N–TiO\(_2\) films. However, an insignificant dissolution of the coating in liquids takes place and leads to the release of nitric oxide from the film into the solution. This can contribute to the activation of biochemical processes in the field of pathology.
3. Results and discussion

The evolution of the coating structure depends on the composition of the working atmosphere and electrical bias. This can be explained in terms of the modified Thornton structural zones model (SZM) for the N-TiO₂ films, which consistently describe the evolution of the film microstructure depending on the nitrogen content in the magnetron discharge [6].

Arrouvel et al. [10] and Labat et al. [11] theoretically studied the structure and energy of the surfaces of nanoparticles of stoichiometric anatase and rutile. These works present the data on structure, relaxation, reconstruction and surface energy of rutile and anatase. It was shown that the crystal planes (101) and (100) of anatase and (110) of rutile are the main planes limiting nanocrystal and determining phase stability [12]. On the crystalline plane (101) of anatase there are both 5 and 6 coordinated titanium atoms (Ti₅C, Ti₆C), as well as 2 and 3 coordinated oxygen atoms (O₂C, O₃C). The surface (100) is limited by both O₂C and O₃C atoms, while the most distant Ti atoms are 5 coordinated. On the surface of rutile (110), two types of titanium atoms and two kinds of oxygen atoms are opened.

Up to date, a number of works [13–15] addressed the adsorption of nitrogen oxides on the surfaces of anatase and rutile crystallites with vacuum leakage of NO, NO₂ gases. The interactions of these surfaces with adsorbed nitrogen oxide molecules are accounted and the optimal positions of their localization are determined. However, the model of the formation of nitric oxide (NO) in TiO₂ films deposited by the RMS method in the process of their growth has not been previously considered.

Figure 1 presents a model for the formation of nitrogen oxides at the grain boundary with the limiting planes (101), (100) of anatase and (110) plane of rutile. From the image obtained by the TEM...
method, it is clear that the grains have a spherical-elliptical shape with a quasi-amorphous interface between them (figure 1(a)). Figures 1(b), (c) and (d) show the grain boundary of the bounding planes (110) of rutile and (101) and (100) of anatase. Nitrogen, being the part of the film, can be located at the interface combining with the oxygen atoms O_{2C} and O_{3C} and forming a nitrogen oxide layer between two adjacent grains. After relaxation of the binding molecules, there is a slight distortion of the crystal lattice of the grains, accompanied by a lateral shift of the oxygen atoms.

The attachment of nitrogen atoms and its oxides leads to displacements of Ti_{1C}, Ti_{3C} and O_{2C}, O_{3C} atoms located both on the surface of the bounding planes and at the interface, and subsequent changes in the anatase and rutile lattice parameters.

4. Conclusions
Our findings show the important role of nitrogen in the evolution of the structure of N – TiO_{2} films deposited by reactive magnetron sputtering. The proposed model of the grain boundary structure shows that nitrogen can be located not only in the interstitial position, but also in the intergrain region, which is even more likely. There it forms a 2D layer of nitrogen oxides, limiting the epitaxial growth of TiO_{2} crystallites in the film structure during reactive sputter deposition. This process determines the “grinding” of the grain structure of the film with increasing nitrogen ratio in the working gas.

The analysis of the results suggests that N-TiO_{2} films under consideration may play the role of nitric oxide depot directly in the field of pathology if they serve as vascular stents coating. Moreover, nitric oxide (NO) is one of the most important molecules in biological systems playing the role of intercellular messenger. Therefore, N-TiO_{2} films may be a novel donor of nitric oxide and become part of a new therapeutic strategy.

The proposed model is confirmed by data on the dissolution of films in liquid solutions, which demonstrate that oxide forms of nitrogen are present both in the initial films and in solutions.

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