The structure of biocoats based on TiO$_2$ doped with nitrogen study

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Abstract. Nitrogen-doped titanium dioxide (N-TiO$_2$) nanofilms were deposited by reactive magnetron sputtering under different bias voltage. The mode of sputtering influences to formation and properties of titanium films. X-ray diffraction (XRD) was used to study the phase transition and crystallinity of the nanofilms. A technique of layer-by-layer measurement of Raman scattering from nanostructured titanium dioxide films based on a preliminary sputtering of the films by argon beam under an angle of 45° and less has been developed. Experimentally confirmed low dissolution rate of the coating in NaCl saline (0.9%).

1. Introduction
Films of titanium dioxide, doped with different elements, found their application in various fields of technology, including medicine. Films for medical purposes are used for many types of implants, including vascular stents, should improve the quality of bar metal stents. The coatings of the stents should have the following properties: biocompatibility, stability of properties and composition, corrosion resistance, that is, reduce the effect on the surrounding tissue [1]. Complex N-TiO$_2$ films are one of the most promising coatings for coronary stents [2, 3]. It is known that such crystalline modifications of TiO$_2$ as anatase and rutile have bioactive properties, manifested in their faster (in comparison with amorphous natural titanium oxide) osteointegration, with preference given to titanium oxide, with anatase structure. Indeed, it has been found that the anatase satisfies, first of all, the crystallographic criteria in the selection of materials for bioactive coatings [4]. The bioactivity of the rutile phase of TiO$_2$ is significantly inferior to the bioactivity of the anatase phase. The necessity of modification of the anatase form of titanium dioxide is due to its use in a number of areas of medicine, where the content of the rutile form is regulated.

In this work we studied N-doped titanium dioxide (N-TiO$_2$) nanofilms obtained by reactive magnetron sputtering by using UVN-200MI laboratory system [5, 6]. The purpose of this work is to investigate the influence of the sputtering conditions, in particular, the bias voltage $U_b$; the influence of the liquid phase, in particular, prolonged contact with the physiological fluid (NaCl saline, 0.9%) on the surface structure of the coating, composition and morphology of the surface of N-TiO$_2$ nanofilms.

2. Experimental part
In the present work the N-TiO$_2$ nanofilms were deposited on the NaCl crystals (plates 10×10×1 mm) and stainless steel substrates using the reactive magnetron sputtering method. The description of laboratory system and using method were given in [5, 6]. The following parameters are used for the nanofilms deposition: cathode material is Ti, operating pressure in the chamber is 0.1 Pa, power is 1.2 kW, current is 3A, working gas leakage rate is 5 ml/min, bias voltage is 0 V and -100 V. The partial pressure ratio of pure plasma-forming gases N$_2$ and/or O$_2$ are p(O$_2$)/p(N$_2$) =1/1, p(O$_2$)/p(N$_2$) =1/3. O$_2$ deposition time is 90 minutes. The X-ray diffraction (XRD) was used to study the structural changes and phase transitions in the nanofilms using XRD-7000 diffractometer (Shimadzu) with grazing angle...
mode (α=1°) under Cu K-α radiation. The average crystallite size was calculated using Scherrer’s equation:

\[ D = \frac{\lambda}{\beta \cos \theta} \]

where \( D \) is the crystallite size, \( \lambda \) is the X-ray wavelength (1.5418 Å), \( \beta \) is the full width at half maximum, and \( \theta \) is the diffraction angle. PDF-4 database of International Center for Diffraction Data (ICDD) was used for the phase analysis (ICDD: anatase #21-1272, rutile #21-1276).

For studying of chemical properties stability the samples were exposed of prolonged interaction with saline (0.9% NaCl), which simulates approximate blood composition of a living organism [7]. The required volume of NaCl solution (4 ml) was determined according to ISO 10993-12 [8]. After 600 days, the samples were removed from solution. The structure of the coatings before and after contact with the solution was investigated by Raman spectroscopy on the Centaur U HR complex [9]. The spectra were measured along the slope of a crater obtained by sputtering an 6 keV argon ion beam with a cross section of 1 mm under an angle of 45° from the bottom of the crater to the surface of the sample. The Raman image of the films was obtained using the Olympus 100 microscope.

3. Results and Discussion

3.1 XRD Analysis

![Figure 1](image-url)

Figure 1. XRD patterns of N-TiO₂ nanofilms deposited at different conditions: grounded substrate \((U_b = 0 \text{ V})\) and negative bias voltage \((U_b = -100 \text{ V})\). A - anatase; R - rutile.

Figure 1 shows XRD patterns of the N-TiO₂ nanofilms obtained at different bias voltage values. As observed in the XRD patterns, the nanofilms deposited at \( U_b = 0 \text{ V} \) consist of 75% rutile and 12% anatase phase mixture. When the negative bias voltage (-100 V) is applied, the films structure changes to a low amorphous/crystalline phase and consists of 78% anatase and 18% rutile mixture including amorphous part. There are some peaks from steel substrate in XRD patterns. The crystallite size (characterized by A (101) and R (110) reflections) is about 14 nm for all nanofilms. As XRD analysis
showed the rutile-anatase transition occurs at the bias voltage mode. The rutile phase volume has decreased from 75% to 18%, while the anatase one has increased up to 78%.

3.2 Raman spectroscopy
The structural and phase characteristics and transitions of TiO$_2$-based films were studied using Raman spectroscopy. Raman spectra of TiO$_2$ are characterized by a set of Ti–O stretching lines in the range (140-800) cm$^{-1}$. In the Raman spectrum, there are six characteristic lines of the anatase phase and four modes of the rutile phase.

![Raman spectra](image)

Figure 2. Raman spectra from films deposited in the atmosphere: 1) O$_2$, 2) N$_2$ + O$_2$ and 3) 3N$_2$ + O$_2$ at a bias potential $U_b$ = 0 V.

Figure 2 shows the Raman spectra of N-TiO$_2$ films formed in the zero-bias potential mode. The films demonstrate a two-phase structure of titanium dioxide (A-anatase, R-rutile). In the Raman spectra, characteristic lines of the anatase phase are observed: 154 cm$^{-1}$ and 405 cm$^{-1}$, and also for the rutile phase: 240 cm$^{-1}$ (two-phonon scattering mode, 2-background). The main anatase peak, observed at 154 cm$^{-1}$, is shifted toward higher wave numbers compared to the single-crystal anatase phase (144 cm$^{-1}$), which may indicate nanoscale structural components of the films. The broadening and decrease in the intensity of the low-frequency maximum also indicates a change in the crystallite size and the degree of crystallinity of the phases.

Figure 3 shows Raman spectra from N-TiO$_2$ films formed at the negative bias potential mode. The spectra contain bands characterized by a mixed structure of titanium dioxide. The blurring of Raman lines may indicate the nanocrystalline structure of the films or their partial amorphization (quasi-morphic structure) [10].
In the Figure 4 the Raman scattering spectrum of anatase, sustained in physiological solution, one can observe two peaks that are located at 144, 640 cm⁻¹, belonging to doubly degenerate modes of optical phonons, and two peaks at 387 cm⁻¹ and 520 cm⁻¹ belonging to nondegenerate modes of optical phonons. The peak of 144 cm⁻¹ is the most informative and most intense. The oscillation frequency (144 cm⁻¹) of samples fabricated at a negative bias (−100 V) mode on a substrate is less intense than for samples deposited in a grounded substrate mode. This type of scattering is related to several reasons, one of which is the quantum mechanical effect of Raman scattering. For the small grain sizes, the phonons of the entire Brillouin zone contribute to the formation of the Raman spectrum, i.e., boundary phonons [11]. This can be explained by the fact that a negative bias voltage $U_b = -100$ V leads to an increase in the amorphous phase, in contrast to the nanocrystalline structure at $U_b = 0$ V. Although the anatase form of titanium dioxide formed with a negative bias voltage applied to the substrate is less stable and can release into solution [7].
We made the Raman scan of the sample surface coated by the N-TiO2 films before and after a long exposure at the solution. The investigation revealed the change of the color and structure of the films, which is due to the change in the morphology and modification of the bio-coating.

4. Conclusions
Nitrogen-doped titanium dioxide films with a dominant phase of anatase were obtained by the method of reactive magnetron sputtering. The influence of the bias voltage on the composition change, the morphology of the surface in NaCl solution of N-TiO2 nanofilms was observed. Negative bias voltage leads to an increase in the anatase phase and the appearance of an amorphous part. The prevalence of anatase in the coating was revealed during prolonged contact with the liquid phase, which confirm of the films corrosion-resistant properties. This property makes the obtained films promising for their use in medicine.

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