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ДОПИНИРОВАНЫЕ АЗОТОМ НАНОПЛЕНКИ ДИОКСИДА ТИТАНА ДЛЯ МЕДИЦИНСКОГО ПРИМЕНЕНИЯ

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В данной работе представлены исследования азотсодержащих нанопленок диоксида титана (N-TiO₂). Исследование нанопленок, рекомендуемых для биомедицины в качестве биопокрытия, вызвано важностью проблемы повышения резистентности медицинских имплантатов. Биопокрытия осаждались методом реактивного магнетронного распыления при различном напряжении смещения U_b = 0-100 V. Допирование азотом оксидной пленки, с технологическим замещением кислорода на атомы азота, меняет свойства материала: проявляются антитромбогенные качества и возрастает уровень гемосовместимости. Повышаются коррозионные показатели пленки. При взаимодействии с биологическими жидкостями происходит частичное растворение биопокрытия с дальнейшим выделением\образованием соединений со связью N-O, которые являются важнейшими соединениями для жизнедеятельности человека. Для исследования фазового перехода и кристалличности нанопленок использовали метод рентгеновской дифракции (XRD). При отрицательном смещении в этих пленках доминирует фаза рутила (68%), объемная доля которого перманентно растет с ростом содержания азота в составе реактивного газа, объемная доля анатаза уменьшается до 10%. Морфология поверхности исследована с помощью сканирующей электронной микроскопии. Установлено, что пленки, осажденные при ненулевых напряжениях смещения, обладают более мелкозернистой структурой, чем при отсутствии смещения. Химическая стабильность и элементный состав оценивали с помощью рентгенофлуоресцентной спектрометрии (XFS) и атомно-эмиссионной спектрометрии (AES). Представлены данные измерений контактного угла и поверхностной энергии. Результаты исследования показали влияние напряжения смещения на фазовый состав, морфологию поверхности и химические свойства нанопленок N-TiO₂. Анализ экспериментальных данных указал, что рассматриваемые пленки N-TiO₂ могут играть роль депо оксида азота непосредственно в области патологии, если они служат покрытием имплантата.

Ключевые слова: нанопленки, диоксид титана, допинирование азотом, химическая устойчивость, анатаз, рутил

NITROGEN-DOPED TITANIUM DIOXIDE NANOFILMS FOR MEDICAL APPLICATION

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The results of study of nitrogen-containing titanium dioxide nanofilms (N-TiO₂) are presented in this work. These nanofilms are used in biomedicine as a biocoating of the implants that is why the problem of increasing resistance is very essential. Biocoatings were deposited by reactive

magnetron sputtering at different bias voltages U_b = 0-100 V. Doping of the oxide film with nitrogen, with technological replacement of oxygen by nitrogen atoms, changes the material properties: antithrombogenic qualities appear and hemocompatibility rates increase. The corrosion resistance rates of the film are also increased. The biocoatings are partially dissolved, when interacting with biological fluids, with a further release/formation of compounds with an N-O bond, which are essential for human activity. X-ray diffraction (XRD) was used to study the phase transition and crystallinity of nanofilms. The rutile phase dominates (68%) when a negative bias in these films was used. The volume of the fraction increases permanently with increasing of nitrogen content in the composition of the reactive gas, while the volume fraction of anatase decreases to 10%. The surface morphology was studied using scanning electron microscopy. It was established that the films have a more fine-grained structure than at the displacement equals zero. Chemical stability and the presence of elements were observed using X-ray fluorescence spectrometry (XFS) and atomic emission spectrometry (AES). The results of measurement of the contact angle and the surface energy are presented. The results of the study showed the influense of bias voltage on the phase composition, surface morphology and chemical properties of N-TiO_2 nanofilms. 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 implants coating.

Key words: nanofilms, titanium dioxide, nitrogen doping, chemical stability, anatase, rutile

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INTRODUCTION

Nanofilms are widely used in recent years in different fields of technologies, especially in medicine [1, 11]. The methods of thin films deposition are commonly in demand for the obtaining of new materials, including nanostructures. The films for medical purposes, used for many kinds of implants and vascular stents, should improve qualities of the products: biocompatibility, stability of properties and composition, reducing the impact on the surrounding tissue [2]. The complex Ti-O-N films are one of the most promising coatings for coronary stents [3, 4, 18, 19].

In this work we have studied N-doped titanium dioxide (N-TiO_2) nanofilms obtained by reactive magnetron sputtering by using UVN-200MI laboratory system [5, 6]. The aim of this work is to investigate the sputtering conditions influence, particularly, the bias voltage U_b = 0-100 V on changing chemical properties, composition, and surface morphology of the N-TiO_2 nanofilms under prolonged contact with physiological liquid (0.9% NaCl solution).

MATERIALS AND METHODS

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, 7]. The following parameters were 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 3 A, 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 O_2 is $p(O_2)/p(N_2) = 1/1$, deposition time is 90 minutes [19].

Influence of deposition parameters on the surface morphology of the N-TiO_2 nanofilms was investigated by the scanning electron microscope (SEM, Philips XL30 ESEM FEG) [9]. The X-ray diffraction (XRD) was used to characterize 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:

$$D = \frac{\lambda}{\beta \cdot cos\theta}$$

where D is the crystallite size, λ is the X-ray wavelength (1.5418 Å), β is the full width at half maximum, and θ 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. The required volume of NaCl solution (4 ml) was determined according to ISO 10993-12 [8]. After 30 days the samples were removed, the solution was filtered through a "blue tape" filter and analyzed for the film elements presence. For this purpose we used X-ray fluorescence (XRF) and atomic emission spectrometry (AES) analyses [10]. Sample with nanofilm not-immersed in NaCl solution was served as a control. XRF spectra were obtained by using X-ray fluorescence analyzer Thermo Electron QUANT'X (EDXRF, USA). The AES analysis was performed using atomic emission spectrometer ICAP 6300 Duo (USA). As standard reference solutions we used the state standard samples (MES-1 and MES-2).

Wettability of the nanofilms were measured by the OCA 15 (Plus Data Physics Instruments GmbH) with sessile drop method, where liquid drop is set on a surface and the contact angle is measured from the drop shape [12,13]. The wetting angle from the interfacial surface tensions was calculated by Young's equation. It describes the interactions between the cohesion and adhesion forces referred as surface energy [14].

The Owens, Wendt, Rabel and Kaelble method (the OWRK) was used for calculating the surface free energy using several liquids such as deionized water (θ_w), glycerol (θ_g), and diiodomethane (θ_d). The OWRK method calculates the surface free energy and its polar (σ^P) and dispersion (σ^D) parts, according to [14].

RESULTS AND DISCUSSION

SEM images illustrated in Fig. 1 demonstrate the surface morphology of the N-TiO_2 nanofilms at 0 V and -100 V. The nanofilms prepared at 0 V have fine-grained structure on the surface (Fig. 1a). It can be obviously observed that the fine-grained structure has changed for a quasi-homogeneous texture of surface (Fig. 1b). The morphology changes and amorphous phase emergence caused by bias voltage are attributed to the ion bombardment managed by substrate bias, according to [9].

Fig. 2 shows XRD patterns of the N-TiO_2 nanofilms prepared at different bias voltage values. As observed in the XRD patterns, the nanofilms deposited at U_b = 0 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 bias voltage mode. The rutile phase volume has decreased from 75% to 18%, while the anatase one has increased up to 78% [17].

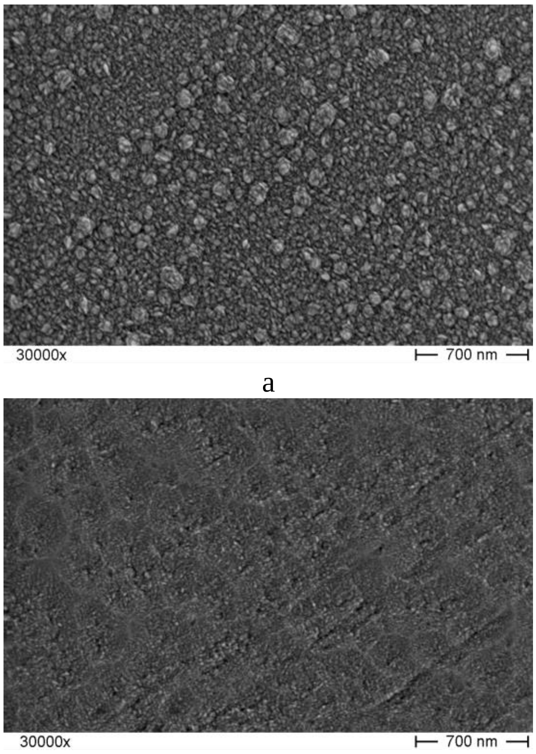

Fig. 1. SEM images of N-TiO_2 nanofilms prepared at 0 V (a) and -100 V (б) bias voltages

Рис. 1. СЭМ изображения N-TiO_2 пленок, полученных при напряжениях смещения 0 В (а) и -100 В (б)

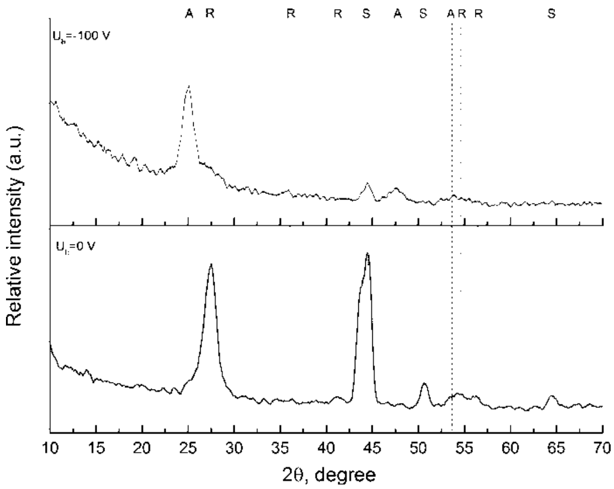

Fig. 2. XRD patterns of N-TiO_2 nanofilms deposited at different conditions: grounded substrate (U_b = 0 V) and negative bias voltage (U_b = -100 V). A – anatase; R – rutile, S – substrate

Рис. 2. Рентгенограммы нанопленок N-TiO_2, осажденных в различных условиях: заземленная подложка (U_b = 0 В) и отрицательное напряжение смещения (U_b = -100 В). А-анатаз, R-рутил, S-субстрат

A typical X-ray fluorescence spectrum of the sample is shown in Fig.3, XRF spectra interpretation – in Table 1[15].

Table 1

The XRF results of the samples after 30 days
***Таблица 1.* Результаты XRF образцов после 30 дней**

Element	Energy of radiation lines E, keV			
	U_b = 0 V		U_b = -100 V	
	film	solution	film	solution
Na	1.04-1.07	1.04-1.07	1.04-1.07	1.04-1.07
Cl	2.5-2.8	2.5-2.8	2.5-2.8	2.5-2.8
Ti	4.5-5	-	-	4.5-5

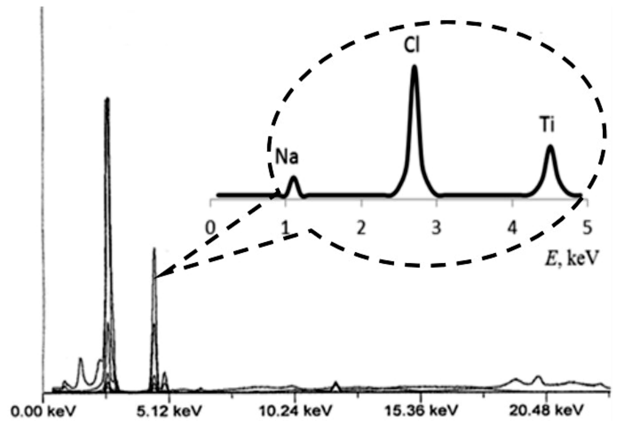

Fig. 3. XRF spectra of the sample
Рис. 3. Спектры ренгенофлуоресцентного анализа образцов

The elements identification of film/solution was performed using the maximum energy of analytical signal [16]. This value on the given spectra equals 2.5-2.8 keV (Table 1**)**, which corresponds to Cl from NaCl crystal (film) and from NaCl solution (solution). The characteristic radiation lines of titanium with energy 4.5-5 keV are intense enough, while the line corresponding to Ti is absent in the spectrum of N-TiO_2 film sample obtained at U_b = -100 V (Table 1). This can be explained by the fact that the negative bias voltage (U_b = -100 V) leads to the amorphous phase growth in contrast with the nanocrystalline structure (at U_b = 0 V), which is not registered by XRF analyzer.

XRF spectrum of the solution after contact with N-TiO_2 film sample obtained at U_b = 0 V is rather different from the XRF spectrum of N-TiO_2 film sample obtained at U_b = -100 V (Table 1). The difference is the presence or absence of titanium characteristic radiation line at 4.5 keV. We suppose that in the first case, titanium being in a more stable rutile form shows chemical resistance -and does not pass into solution from the sample surface. While the anatase form of titanium dioxide formed at the negative bias voltage applied to substrate is less stable and can pass into solution [20].

The presence of Na and Ti ions in solution were proved using AES analysis (Table 2). AES results as well as XRF indicate expected high Na concentration in the solution, and trace amounts of titanium (at U_b = -100 V) which confirm our assumption about the possibility of Ti yield into solution from the N-TiO_2 nanofilm.

Table 2

The AES results of the samples after 30 days
***Таблица 2.* Результаты AES образцов после 30 дней**

Deposition modes	Average value of the element concentration in the test solution, mg/l	
U_b,V	Na	Ti
0	119600	0
-100	120500	0.0039

Table 3

Contact angle and surface energy data of the nanofilms
***Таблица 3.* Данные об угле контакта и поверхностной энергии нанопленок**

Sample	θ_w (deg.)	θ_g (deg.)	θ_d (deg.)	σ (mN/m)
N-TiO_2 0V	116±0.2	108±0.4	70±0.2	20±0.8
N-TiO_2 -100 V	92±0.2	104±0.4	68±0.1	20±0.6

Table 3 presents the data of contact angle and surface energy measurements. It can be seen that the negative bias does not influence the surface energy values. The water contact angle of N-TiO_2 nanofilms deposited at -100 V decreased up to 92 degrees. Probably, it can associate with different surface topography.

CONCLUSIONS

Thus, the bias voltage influence applied to substrate on changing of the composition, the surface morphology, and chemical stability in NaCl saline of the N-TiO_2 nanofilms was found out. The negative bias voltage leads to the anatase phase increasing and amorphous part emergence. The fine-grained surface morphology changes to the quasi-homogeneous texture. By means of modern spectroscopic methods of analysis (XRF, AES) it is proved corrosion-resistant properties of N-TiO_2 film obtained at U_b = 0 V and does not change the qualitative and quantitative composition of the saline. Both methods of analysis are in good agreement with each other.

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