CHARACTERIZATION OF NITROGEN-CONTAINING TITANIUM DIOXIDE THIN FILMS BY X-RAY DIFFRACTION AND IR SPECTROSCOPY TECHNIQUES

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ХАРАКТЕРИСТИКА АЗОТСОДЕРЖАЩИХ ТОНКИХ ПЛЕНОК ДИОКСИДА ТИТАНА МЕТОДАМИ РЕНТГЕНОВСКОЙ ДИФРАКЦИИ И ИК-СПЕКТРОСКОПИИ

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В работе приводятся результаты исследования структуры и химического состава азотсодержащих тонких пленок диоксида титана, осажденных методом реактивного магнетронного распыления. Приведены результаты анализа изменения структуры и фазового состава тонких пленок диоксида титана при увеличении содержания азота в газовой смеси методом рентгеновской дифракции. Химические связи, присутствующие в пленках, исследовались методом ИК-спектроскопии.

Titanium dioxide thin films are widely used in diversified fields of application such as building materials, cosmetics, pigments, solar cells and biomaterials due to their outstanding properties [1]. The film properties can be controlled by changes of their structure. Most of the experimental efforts have focused on the nitrogen incorporation and determination of its location into the film crystal structure [2].

The aim of this work is to determine the influence of the nitrogen doping on the TiO_2 structure. The attention has been focused on crystallinity, chemical composition and chemical bonds of N-TiO_2 films.

N-containing titanium oxide (N-TiO_2) thin films were deposited on stainless steel substrates (*12Cr18Ni10Ti*) using homemade magnetron sputtering system UVN-200MI (Tomsk Polytechnic University). The oxygen (in case of TiO_2) and the mixture of oxygen and nitrogen with different ratios (in the case of N-TiO_2) were used as working and reactive gases. A commercially pure titanium (Ti) *VT-1.0* was used as target for sputtering. The deposition parameters were the following: working pressure in the chamber: 0.1 Pa, current: 3 A, power: 1 kW, working gas in-leakage rate: 5 ml/min. The partial gas pressure ratio $p(O_2)/p(N_2)$ was 1/1 or 1/3.

The structural characterization of N-TiO_2 films was carried out by Bruker D8 Advance X-ray diffractometer (XRD) in $\theta/2\theta$ geometry. All the samples were measured in the continuous scan mode in the 2θ range of 10–70°. Measurements were obtained at 40 kV, 20 mA with a Cu-Kα radiation (λ= 0.15418 nm), a step size of 0.02°. For the phase analysis of the thin films the PDF-4 database of International Center for Diffraction Data (ICDD) was used. The crystallite size was calculated using the Scherrer equation.

The elemental analysis of these films was carried out by using an energy dispersive X-ray analysis (EDS analysis system Genesis 4000). The chemical bonds that were present in the films were detected using infrared

spectroscopy (IR). Optical absorption spectra were obtained with the use of a Termo Nicolet 5700 spectrometer in the range 400–4000 cm^{-1}.

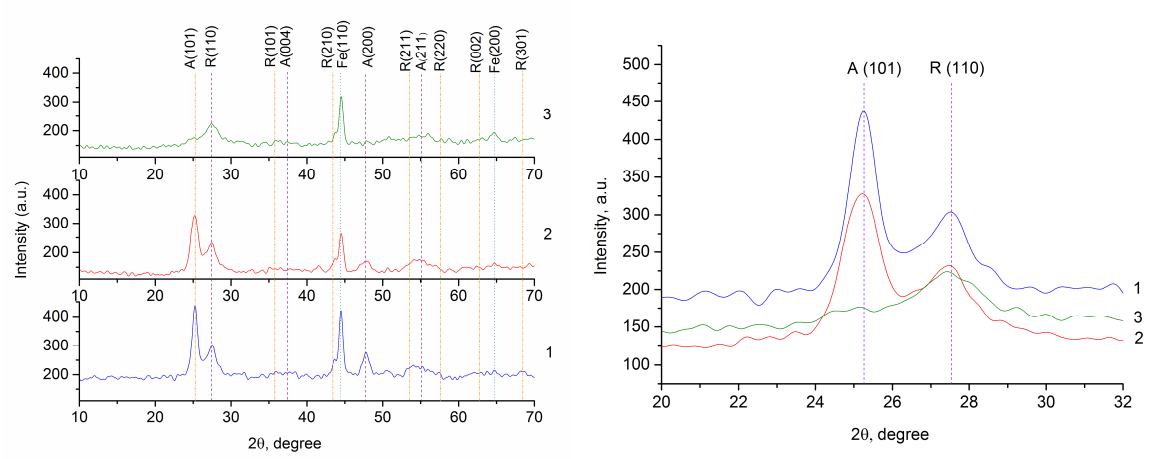
Three groups of samples were used for the study. These groups and the data of elemental composition are represented in Table 1.

Table 1

Elemental composition of N-TiO_2 thin films

Sample	N, at.%	O, at.%	Ti, at.%
#I TiO_2	-	84.41	15.59
#II Ti-O-N (1/1)	5.71	80.27	14.02
#III Ti-O-N (1/3)	6.16	80.01	13.83

The X-ray diffraction patterns of N-TiO_2 films shown in the figure 1 (a) illustrate the changing of the crystal structure of the films as a function of the N content. The films consist of the mixture of anatase and rutile with tetragonal structure (see figure 1), and there are some peaks from substrate material (α-Fe, body-centered cubic). Regardless of the substituted nitrogen concentration, there is no presence of TiN phases. Increasing of the amount of incorporated nitrogen leads to decreasing of the share of anatase phase and increasing of rutile ones. The XRD analysis of N-TiO_2 films shows that the increase of N concentration in the film changes the intensity of diffraction peaks (Fig.1 (b)). This can be associated with the changing of the phase composition of the films. The broadening of anatase (101) and rutile (110) peaks occurs with the increase N concentration (Fig.1 (b)) also. This can be explained by the decrease of crystallite size and presence of microstrains [3].



a *b*

Fig. 1. XRD diffraction patterns of N-TiO_2 films as function of nitrogen content: 1 – N = 0; 2 – N = 5.71 at.%; 3 – N = 6.16 at.%

The calculation of the crystal size showed the reduction of crystallites from 15 nm to 8 nm with the nitrogen increase. The amount of anatase decreases from 60% to 22% while as the amount of rutile increase from 38% to 68% with the nitrogen increasing.

The FT-IR spectra of N-TiO_2 are shown in Fig. 2. The bands between 464 and 530 cm^{-1} are attributed to the vibration of Ti–O–Ti bond [4].The peaks in the range of 700-705, 791-796, 1370-1390 cm^{-1} corresponds to Ti-O stretching and Ti-O-Ti bridging stretching modes [5]. The weak peak at around 1300 cm-1 is observed in the spectra of N-doped samples, which can be attributed to N-O stretching vibration [5].

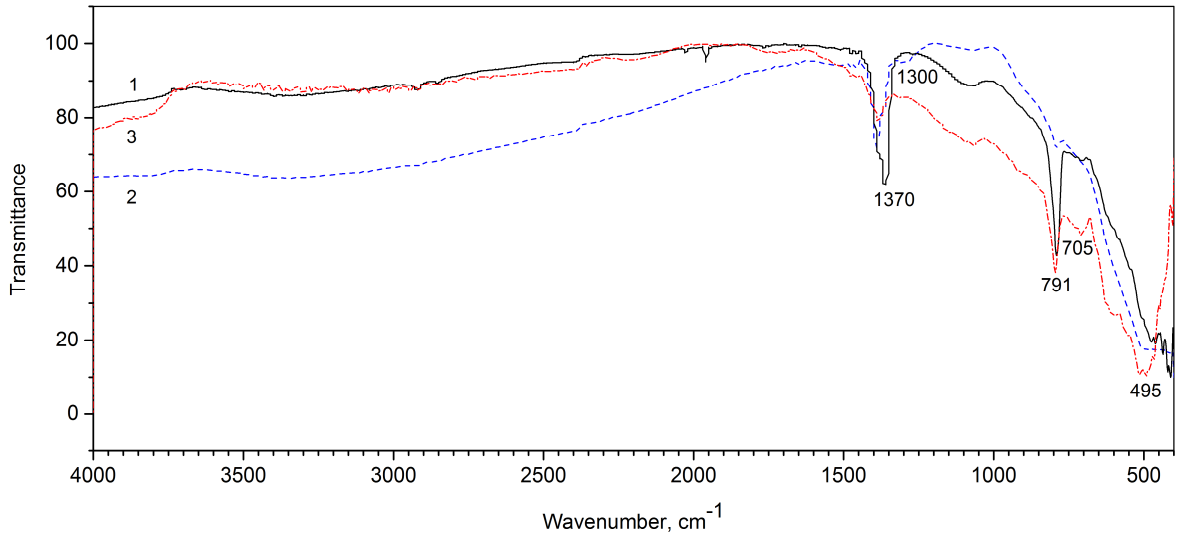


Fig 2. FT-IR spectra of three groups samples: 1 – #I TiO_2; 2 – #II Ti-O-N; 3 – #III Ti-O-N

Thereby, the incorporation of nitrogen in the TiO_2 lattice leads to the structural changes of the films. The transition from anatase to rutile takes place, and the crystallites size reduced due to an increase in nitrogen concentration.

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