Technical Physics Letters, 2022, Vol. 48, No. 13

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Effect of low temperature nitrogen plasma composition on hydrophilic and hydrophobic properties of coatings nitrided titanium oxide based

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Received May 6, 2021
revised June 18, 2021
accepted June 26, 2021

Effect of nitrogen plasma composition on structural-phase and elemental composition, topography, mechanical and hydrophobic properties of coatings on the basis of nitrogen-containing titanium oxide during penetration onto sample in open atmosphere is studied. It has been shown that at an equally high microhardness of the order of 25–27 GPa, by controlling the composition of the nitrogen plasma, either hydrophilic (contact angle 73°)) or hydrophobic coatings (contact angle 120°)) can be formed.

Keywords: hydrophobicity, hydrophilicity, titanium dioxide, sapphire, low-temperature plasma, nitrogen, contact angle, microhardness.

DOI: 10.21883/TPL.2022.13.53355.18861

With the development of modern technology, the need for titanium-based compounds and alloys has increased significantly. Those in the highest demand among them are polymorphic modifications of titanium dioxide (TiO_2). Titanium dioxide has a high reflection coefficient and radiation resistance [1] and can be used to protect spacecraft from solar radiation. Modifying the surface of titanium implants by applying layers of titanium dioxide increases biocompatibility and even makes the surface bioactive [2]. This effect can be enhanced by nitrogen doping of titanium dioxide. For example, the authors [3,4] have shown that coatings based on titanium nitrides, oxynitrides can improve antithrombogenic properties of cardiovascular implants. In this case, one of the main requirements is the high hydrophilicity of the titanium dioxide coating surface, which causes its strong interaction with blood and faster osseointegration. In contrast, the application of titanium dioxide to photocatalytic purification processes [5] requires complete immobilization of the purifier surface in relation to the environment, such as water molecules. The surface of titanium dioxide should be as hydrophobic as possible to minimize adsorption of water molecules and active decomposition of molecules of harmful substances.

Consequently, the use of titanium dioxide coatings is expected in a variety of conditions, and this dictates special requirements to their mechanical properties. In study [6] the possibility was demonstrated of obtaining super hard coatings based on titanium dioxide by processing it in low-temperature nitrogen plasma in open atmosphere. As for the physical interaction with liquids, it is assumed that high sorbability of OH-groups by the surface of titanium dioxide [7] makes it hydrophilic. However, along with chemical properties, hydrophilic properties can be strongly influenced by surface roughness, micromorphology [8] and monophase nature [9], as it turned out. In study [9] it is shown that, depending on phase composition, completely opposite states can be realized on titanium dioxide surfaces of similar roughness: monophase surface is characterized by high hydrophobicity, and in case of mixed (anatase, rutile) composition such surface becomes hydrophilic. In addition, the effect of nitrogen doping on hydrophilic and hydrophobic properties of titanium dioxide-based coatings has been demonstrated in several studies [10,11]. An interesting result [10] was obtained: the increase in hydrophobicity achieved by the formation of a specific morphology in the form of rutile phase nanorods was leveled by an increase in nitrogen concentration above 7%, despite the fact that observably it kept strengthening only while nitrogen was building up to 3%. A hydrophilic state was realized in solid titanium dioxide films of mixed phase composition with low level of nitrogen doping (less than 0.1%).

The above data indicate the dependence of hydrophilic properties of titanium dioxide films on their structural-phase and impurity composition, surface roughness and morphology. We believe the technique of titanium film processing in nitrogen plasma in an open atmosphere exploited in [6] can be optimal in forming titanium dioxide coatings of specified properties (hydrophilic or hydrophobic), provided the plasma composition is controlled. Meanwhile, another requirement is to produce super hard coating. The present study explores the effect of low-temperature nitrogen plasma composition flowing over the sample in an open atmosphere on the structural-phase and elemental composition, topography, mechanical and hydrophobic properties of coatings based on nitrided titanium oxide.

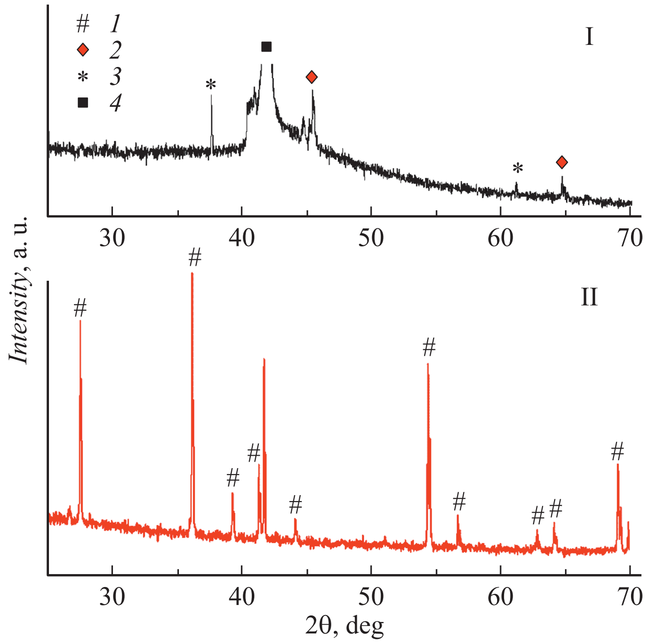

Figure 1. X-ray diffraction images of type I, II samples. ICSD database (PDF-2), card number 98-002-4277. *1* is rutile, *2* is brucite, *3* is anatase, *4* is sapphire.

A titanium film about 500 nm thick was deposited on sapphire substrates by magnetron deposition [8]. The substrate was preheated to 200°C. The magnetron deposition method improved the adhesion between the film and the substrate due to high energy of plasma ions and plasma activation of the surface. Next, samples were treated with a stream of low-temperature high-enthalpy nitrogen plasma in an open atmosphere. A DC plasma torch with vortex stabilization and an expanding output electrode channel [11,12] was used as a nitrogen plasma source. Samples were treated in an open atmosphere using nitrogen plasma with a mean mass temperature of 4−5 kK (type I sample hereinafter) and 7−9 kK (type II sample hereinafter). According to the data available [13] we can analyze the difference in the composition of plasmas (per 1 cm^3): in type I plasma molecular nitrogen N_2 was predominant by the factor of 10^4; the ratio of ionized nitrogen molecules N^{2+} is the same in both plasmas; in type II plasma atomic nitrogen N is predominant by the factor of 10 and that of ionized nitrogen atoms N^+ by 10^3. Processing time was 1 min. X-ray images were taken using an Empyrean diffractometer by PANalytical (Netherlands) in Bragg–Brentano geometry. The obtained X-ray images were processed using HighScore Plus (PANalytical) software, and the phase analysis was performed using the ICSD database (PDF-2). Copper anode radiation was used (Cu$K_{\alpha 2}$, $\lambda = 1.54$ Å). Microscopic studies were carried out on a JEOL scanning electron microscope equipped with an energy dispersive X-ray microanalyzer, and an atomic force microscope Solver Pro-M. The RMS roughness was determined using the Nova software included in the instrument package. Samples hardness was examined using a scanning nanohardness meter NanoScan-3D. Microhardness of samples was determined by dynamic indentation. The Vickers microhardness was calculated averaging the number of indentations in the area of $50 \times 50\,\mu$m with a load from 1 to 50 mN. Surface hydrophobicity analysis (measurement of contact angle ϑ) of the samples was carried out using the sitting drop technique. The water drop was about 1.5 mm in size. The contact angle was measured 10 s after the droplet was applied and reached immobility. Optical imaging was performed using a digital camera. The axis of the camera lens was placed at the water drop–sample surface interface. The contact angle was determined according to the method described in [14].

Results of analysis of the diffractograms obtained from the samples is shown in Fig. 1. It can be seen that type I film sample is an X-ray amorphous oxidized precipitate with the possible presence of a small fraction of anatase, brucite. A polycrystalline rutile monophase is formed in the sample of type II film. According to the data of scanning electron microscopy (Fig. 2), the surface of type I film is represented by two types of structures: faceted crystallites sized up to a micrometer and porous structures with rounded edges. In the sample of type II film, faceted crystallites with sizes up to several micrometers were mainly observed. According to energy dispersive X-ray microanalysis (see Table), the content of nitrogen and oxygen in type I film was significantly lower than in type II film. Samples also differed significantly in their roughness

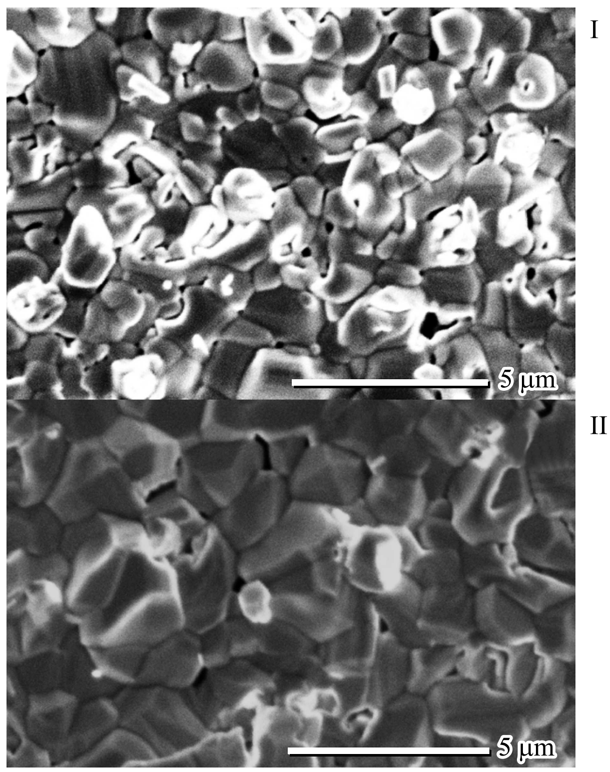

Figure 2. Electron microscopic images of sample surfaces, type I, II.

Element (atomic) ratios, roughness (R_q), microhardness (H) of nitrogen-containing titanium oxide films on sapphire produced in two modes (type I and II samples)

Parameter	Type I	Type II
Ti/N	4.46	1.92
O/Ti	4.94	7.34
R_q, nm	136.4	71.4
H, GPa	25.5	27

value (see Table). Microhardness was investigated by averaging over the number of indentations in the range of imprint depths 50−200 nm. The values of 25.5 and 27 GPa were obtained for type I and II films, respectively. The sitting-drop study showed the most interesting result: the surface changed its state from hydrophilic ($\vartheta = 73^\circ$) to hydrophobic ($\vartheta = 120^\circ$) when changing from type I to type II sample (Fig. 3).

The obtained results point to significant differences in oxidation and crystallization that titanium film undergoes forming on sapphire substrate in dependence of the processing conditions. Apparently, when treated in plasma with ionized nitrogen atoms, all processes occur exclusively in the solid phase. The high mean mass temperature (7−9 kK) of plasma contributes to a rapid heating of the surrounding atmosphere entailing high activity of oxygen along with ionized nitrogen atoms. X-ray diffraction image (type II in Fig. 1) and electron microscopy data (type II in Fig. 2) indicate the course of solid-phase crystallization processes in the oxide film: the required temperature, concentration saturation with active oxygen and high diffusion activity are achieved. It was not possible to realize solid-phase crystallization processes with the formation of a highly oriented rutile film, because a longer plasma treatment resulted in destruction of the substrate.

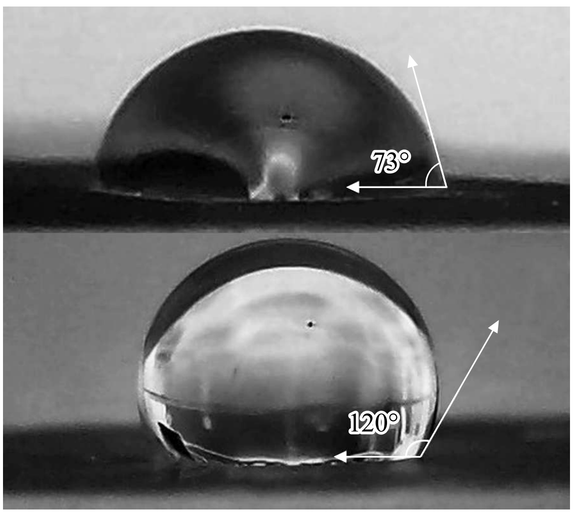

Figure 3. Dependence of hydrophilic and hydrophobic properties of samples on processing conditions.

In their turn, the rounded porous formations on the surface of the type I sample (Fig. 2) treated in the mode of molecular plasma (mean mass temperature 4−5 kK) testify to partial presence of the liquid phase. Titanium has a fairly high melting point (1670°C), but the relatively low reactivity of oxygen and molecular nitrogen ions prevents the titanium film from skipping melting stage. The lag of titanium oxidation from its melting and the decrease of titanium density in the liquid phase can explain the formation of pores and caverns in the film. The presence of such topographic inhomogeneities is associated with an increase in the roughness of the type I film compared to that of type II film (see Table). The microanalysis data (see Table) indicate a decrease in concentration of oxygen and nitrogen in type I film, which is quite logical if we consider low reactivity of gases of molecular composition. The lack of strong differences in microhardness of the samples, despite their significant structural-phase and morphological difference, draws attention. Apparently, one of the main reasons for the increase in microhardness of coating are the internal compressive stresses associated with peculiar surface processing: the oxidation front advances fast from the coating surface into its depth. Note the increase in roughness of sample treated in type I mode. It is quite possible that an increase in hydrophilic surface roughness leads to a decrease in its contact angle, as the Wenzel–Deryagin model stipulates. However, the observed results cannot be explained by surface roughness alone, since a radical change in surface properties from hydrophilic to hydrophobic requires a change in the roughness structure itself, in particular, a transition to multimodal roughness. As studies show, the concentration of nitrogen in the two types of coating differs by a factor of more than 2 (see Table). According to calculations [15], nitrogen doping of TiO_2 clusters raises the positive Gibbs adsorption energy and the hydrophobic component. In general, results of our studies confirm the conclusions drawn in [9]: the monophase film of type II with rutile structure is highly hydrophobic; X-ray amorphous film of type I exhibits hydrophilic properties. According to the data from [16] crystalline monophase can contribute to the formation of an ordered molecular monolayer of carboxylic acids with pronounced hydrophobic properties on the surface of titanium dioxide.

In this study we considered the effect of composition of nitrogen plasma flowing on the substrate surface in an open atmosphere on mechanical and hydrophobic properties of coatings based on nitrogen-containing titanium oxide. It was shown for the first time that by controlling the composition of the nitrogen plasma, it is possible to form either hydrophilic or hydrophobic coatings based on nitrogen-containing titanium dioxide of high microhardness.

Funding

Studies were carried out within the scope of state assignment to the Federal Research Center „Crystallography and Photonics“ of the Russian Academy of Sciences (RAS) on characterization of samples; state assignment to FGBU OIVT RAS on nitrogen plasma exposure effects, and the support of the Russian Foundation for Basic Research (grant № 20-0800598). X-ray phase analysis of the coating was carried out with partial support of government assignment FZNZ-2020-0002.

Conflict of interest

The authors declare that they have no conflict of interest.

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