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INVESTIGATION OF OPTICAL AND ELECTRICAL PROPERTIES OF TITANIUM OXYNITRIDE FILMS

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Abstract. In this work, titanium oxynitride films were obtained on the surface of glass and silicon substrates by magnetron sputtering in a mixture of argon-oxygen-nitrogen gases. The thickness of the obtained films, their deposition rate, and surface morphology were estimated depending on the type of substrate. The optical and electrical properties of films produced on the glass surface have been studied. A comparison of optical data with literature data showed the formation of amorphous films with a composition close to the stoichiometric composition of $TiO_{1.27}N_{0.49}$. The results showed that the obtained properties correspond to the literature data, which opens up new prospects for the use of the obtained titanium oxynitride films as an active element of memristors, and in other important areas of modern materials science.

Keywords: Titanium oxynitride, thin films, magnetron sputtering, absorption spectrum, electrical resistivity.

1. Introduction

Currently, memristors are one of the promising areas for creating an element base for use in neuromorphic applications and as elements of non-volatile memory [1-3]. The first experimental results on the manufacture of memristors were obtained on the basis of thin films of titanium dioxide TiO_2 [4]. Further, in the course of numerous research works, memristors based on various inorganic and organic materials were obtained. Fairly large number of inorganic materials with a memristive effect are known: oxide materials such as TiO_x, HfO_x, AlO_x, TaO_x, VO_x etc., oxides of rare earth metals: Y, Ce, Sm, Gd, Eu, Pr, Er, Dy, and Nd; perovskites: $SrTiO_3Ba_{0,7}Sr_{0,3}TiO_3$, $SrZrO_3$, $BiFeO_3$, as well as metal nitrides [5-8].

Titanium compounds such as titanium oxide and titanium nitride are materials on which a memristive effect is obtained or used as electrodes for memristors [4, 9, 10]. Memristors based on titanium oxynitride (TiO_xN_y) were also obtained in [11]. Titanium oxynitride occupies an intermediate state between titanium oxide and titanium nitride in its physico-chemical properties. It is possible to obtain materials similar in properties to titanium oxide or titanium nitride by changing the concentration of oxygen and nitrogen in TiO_xN_y films. Memristors based on titanium dioxide films with an admixture of copper were manufactured in [12]. Modification of films with copper leads to a significant improvement in the basic memristive characteristics compared with titanium dioxide-based storage devices. It is shown that the use of these films in the memristor structure makes it possible to increase the ratio of the state with high electrical resistance to the state with low electrical resistance by more than 10^2 times.

Recently, interest in titanium oxynitride films has been growing as a promising material for use in biomedical applications [13], for photocatalysis [14] and as plasmonic materials [15]. Various synthesis methods are used such as pulsed laser deposition [14], magnetron sputtering [16] ion beam deposited [17] low-pressure metal-organic CVD [18] etc. Despite numerous studies in this area, there are issues that, when considered, will allow us to optimize the technology for producing thin films of titanium oxynitride and better determine their physical and chemical properties.

In this paper, the optical and electrical properties of thin titanium oxynitride films obtained by magnetron sputtering are investigated. During the production of films, a mixture of oxygen and nitrogen gases was introduced into the volume of the working chamber simultaneously with argon in proportion to their concentration in the atmosphere. This suggests that titanium oxynitride films can be produced using the addition of a small volume of air.

2. Materials and experimental details

The magnetron sputtering method was used for obtaining titanium oxynitride films. It was used a modernized NNV-6.6-I1 installation [19]. The installation was equipped with a plasma source with a hot cathode "PINK" and a dual magnetron sputtering system with two planar magnetrons and targets. The targets with a diameter of 100 mm are made of titanium grade VT-01. Preliminary, prepared samples were placed in the installation chamber on a rotating substrate holder. Vit-3 vacuum meter was employed for pressure control in the chamber. The chamber was evacuated for an hour until a vacuum of 10^{-3} Pa was achieved. Then argon gas was pumped into the chamber and a pressure of 10 Pa was achieved using the gas leakage system. After switching on the "PINK" the samples were cleaned in argon plasma for 5 minutes. Then the argon pressure was reduced to 10^{-2} Pa, and the dual magnetron was switched on in pulse mode with a frequency of 30 kHz. The targets were "burned" for 2-5 minutes until stable parameters for current (1.17 A) and voltage (522 V) of discharge combustion were reached. This was indicated by the absence of microarcs on the target. Then, in addition to argon, a mixture of oxygen and nitrogen gases was introduced into the system using a needle-type manual leak in the proportion of 4 parts nitrogen (N_2) and 1-part oxygen (O_2).

The magnetron operated in the direct current mode. The gas feed rate increased until the discharge voltage began to grow. The gas flow rate was fixed and the rotary table with the substrates fixed on it was turned on. The substrate rotation speed was maintained constant. The thickness of the deposited layer on the substrate depended on the deposition time and the magnetron discharge power. The coatings were deposited for 15 minutes at a rotation speed of 2 revolutions per minute, with a discharge power of 0.6 kW. Air was let into the chamber and the deposited samples were removed when the deposition process was completed.

Cover glasses and silicon plates were used as substrates. The described method yielded 5 films on cover glasses and 2 films on silicon plates. The resulting films were golden in color, which is one of the proofs of the realization of the synthesis of titanium nitride TiN or titanium oxynitride films (TiO_xN_y). To determine the thickness of the obtained films, the substrates were weighed before the film was applied and with the resulting film on an electronic scale RADWAG AS 60/220.R2 [20]. The film thicknesses were estimated based on tabular values of TiO_xN_y material densities [21].

The dependence of the film density on its composition was constructed to estimate the density of titanium oxynitride films in Figure 1, Supplementary Material (SM). This graph contains extreme points in the form of titanium nitride (5.43 g/cm^3) [22] and amorphous titanium oxide films (3.0 g/cm^3) [23]. The density of titanium oxynitride films (4.25 g/cm^3) was taken as an intermediate value [24]. The film composition was established by comparing the absorption coefficient of the films (α) from the wavelength of light with the literature data.

Data on the substrates used, and the average values of the thicknesses of the films obtained and the deposition rates are shown in Table 1. Sample number 1 was submitted for surface properties studies using electron and probe microscopy methods, therefore optical and electrical studies were carried out with samples 2-4.

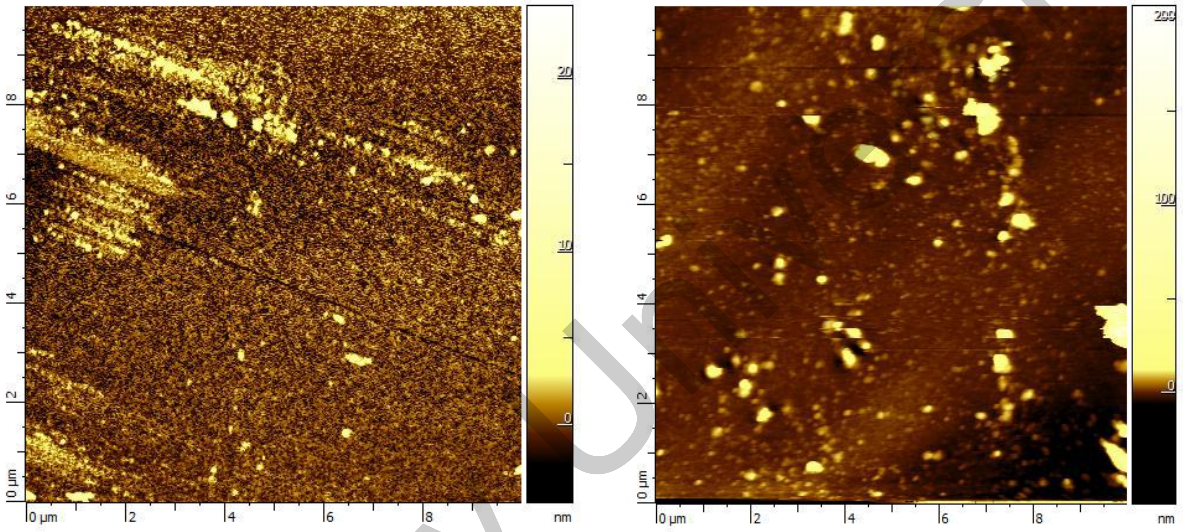
Table 1. Main characteristics of the obtained films and the process of their application.

Substrate material	Substrate area, cm^2	Film thickness, nm	Film spraying rate
Cover glass	3.28	91.9 ± 1.7 (P= 0.95)	6.13 nm/min
Silicon substrate	1,54	244.3	16.3 nm/min

The morphology of the films was studied using a NIST-NT atomic force microscope and a Hitachi 3030TM scanning electron microscope (SEM). The composition of the films was measured by EDX (Energy dispersion X-Ray spectroscopy) on a Hitachi 3030TM SEM. The optical properties of the films were studied using a Solar CM2203 spectrofluorometer. The electrical resistance of the films was measured using a two-probe method according to the method [25].

3. Results and discussion

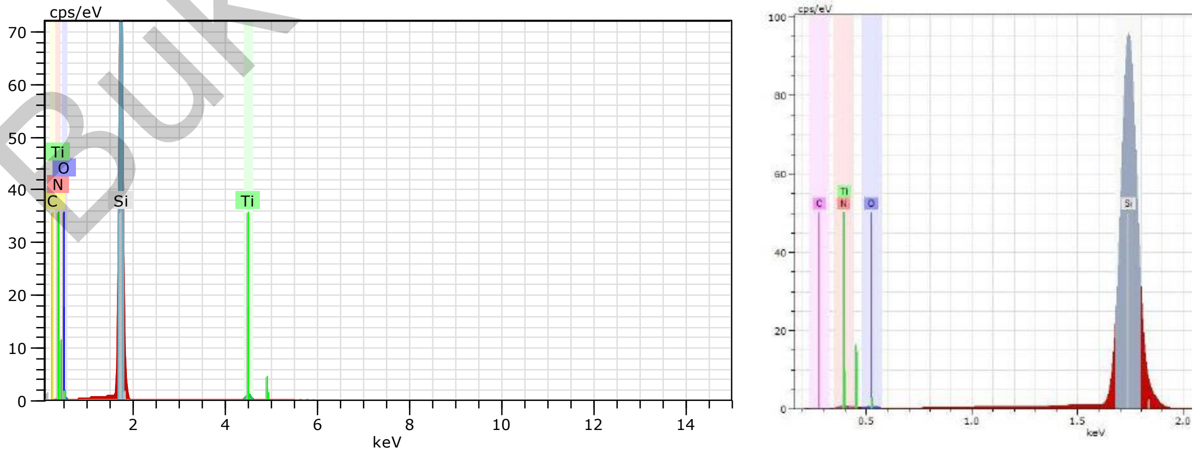
The surface morphology of the obtained TiO_xN_y films is shown in Figure 1. The films obtained on silicon is fine-grained with a uniform grain distribution (Figures 1, a). The film on glass has large grains unevenly distributed over the surface in addition to small grains. Thus, the film obtained on the silicon surface has a less rough surface. The side view for the films is shown in Figure 2, SM. The results of the study of the morphology of the surface of the obtained films on SEM showed the absence of visible microdefects (Figure 3, SM).



a) b)

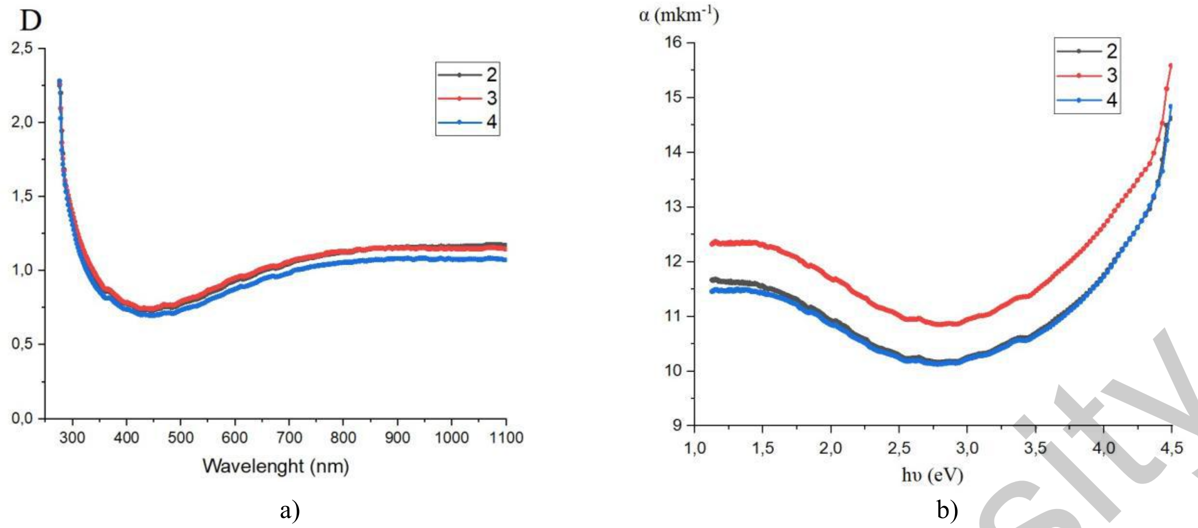
Fig.1. AFM images of films with an area of 10 × 10 µm obtained on a silicon surface (a) and on a glass surface (b).

The results of film composition measurements by the EDX method on silicon substrates are presented in Figure 2. The spectrum contains small peaks corresponding to the characteristic radiation of the elements Ti, N, O, and the main peak belongs to silicon since the obtained films are thin.



a) b)

Fig.2. EDX spectra of a film sample on a silicon surface:
a) full spectrum; b) enlarged fragment in the range up to 2 keV

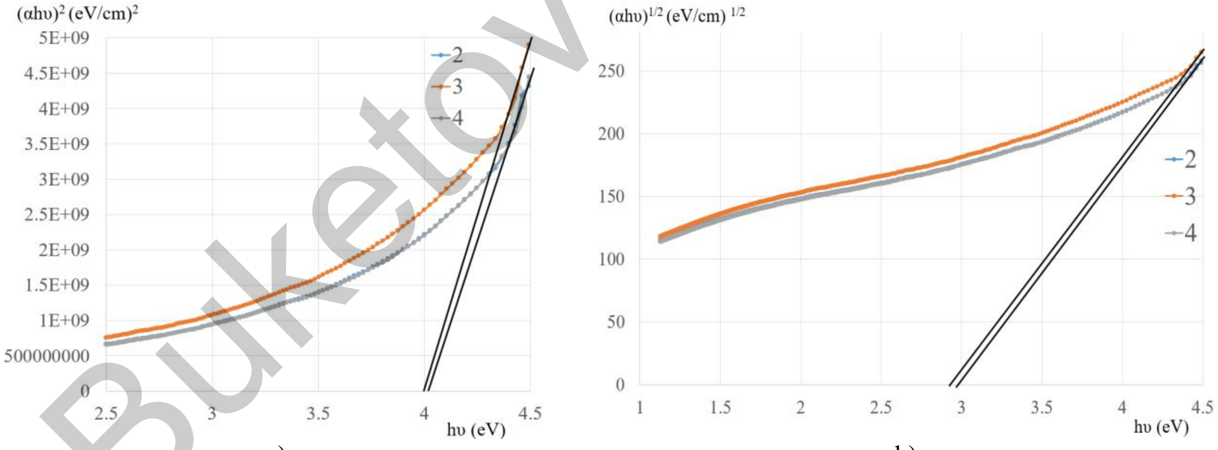


a) b)

Fig.3. The absorption spectrum of films (a) and the dependence of the absorption coefficient (α) on energy.

The EDX spectra confirmed the presence of titanium (peaks corresponding to energies of 0.4, 4.5 keV, etc.), nitrogen (0.3 keV), and oxygen (0.5 keV). The content of the elements by weight (wt.%) above 1% (measurement error). This allowed us to conclude that the Ti, N and O elements are present in the film.

The distribution map of the elements over the sample surface is shown in Figure 4, SM and the distribution maps of each element separately are shown in Figure 5, SM. The data obtained show that the distribution of all elements over the film surface is uniform. Figure 3, a, b shows the absorption spectra of several films on the surface of cover glasses. The spectral curves show an increase in optical density in the wavelength range from 450 nm to 1100 nm, Figure 3, a, which corresponds to energy values from 2.7 eV to ~ 1.1 eV. A comparison of the spectra obtained in the work (Figure 3, a, b) with the literature data [14, 15] shows that the studied films have an amorphous structure [14] and are similar in properties to samples with the stoichiometric composition $TiO_{1.27} N_{0.49}$ [15].



a) b)

Fig.4. Dependency graphs $(\alpha h\nu)^2 = f(h\nu)$ (a) and $(\alpha h\nu)^{1/2} = f(h\nu)$ (b).

The graphs of the dependences of $(\alpha h\upsilon)^2$ and $(\alpha h\upsilon)^{1/2}$ on the parameter hυ are shown in Figure 4. As a result, the values of the band gap were obtained for these graphs: for the graph $(\alpha h\upsilon)^2$/ hυ, the value Eg ~ 4.0 eV was obtained, for the graph $(\alpha h\upsilon)^{1/2}$/ hυ − Eg ~ 2.8-2.9 eV. The value of the optical band gap Eg = 4.12 eV was shown in [26] for nanocrystalline TiN_xO_{1-x} films. This result was obtained from the graph of the dependence $(\alpha h\upsilon)^2$ / hυ. Therefore, this result indicates the synthesis of titanium oxynitride films. However, in [14], the values of the band gap for films of 1.60 eV-1.64 eV were obtained. Therefore, this issue requires further research. It should also be emphasized that similar values of the band gap were obtained for TiO_2 films of the crystalline modification of brookite Eg> 3.5 eV for the $(\alpha h\upsilon)^2$/ hυ graph (direct allowed transitions of TiO_2) and Eg ~ 2.9-3.2 eV for the anatase and rutile modifications of titanium dioxide (indirect allowed transitions) [27]. The difficulty in determining the optical band gap of titanium oxynitride may be due to the fact that titanium oxynitride is represented predominantly by the amorphous phase of this substance. This is indicated by a comparison of the data in the Figure 3, a with the literature data [15].

The electrical resistivity of TiO_xN_y films was measured using a two-probe method (Figure 5). The data obtained for some samples are shown in Table 2. A comparison of the values of specific resistance obtained in the work with literature data was carried out. The results of the comparison showed that the specific resistance of the obtained films is in good agreement with the available literature data [28-30]. In this case, the obtained values of the electrical resistivity of the films corresponded more closely to the values of the resistances of titanium nitride TiN_2 films than titanium oxide TiO_2.

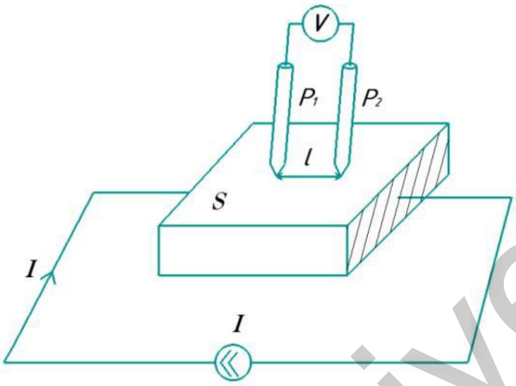


Fig.5. Scheme of measuring specific resistance using the two-probe method:
I - the current flowing through the film under study, S - the area of the films; l - the distance between the probes;
U - the measured voltage between the probes.

Table 2. Electrical resistivity of TiO_xN_y films

№, sample	I (mA)	S (m^2)	L, (cm)	U (V)	ρ (Ohm*cm)
2	1.4	$0.18*10^{-6}$	0.4	0.707	$0.227*10^{-3}$
3	1.4	$0.17*10^{-6}$	0.4	2.38	$0.7225*10^{-3}$
4	1.4	$0.18*10^{-6}$	0.4	2.396	$0.766*10^{-3}$

Thus, the conducted studies have shown that in the process of magnetron deposition of titanium in a working chamber with a mixture of argon, nitrogen and oxygen gases, titanium oxynitride films with an amorphous structure were obtained. Analysis of the optical and electrical properties of the obtained films showed that these data correspond to literature data.

4. Conclusion

In this work, thin films of titanium oxynitride on glass and silicon substrates were obtained by magnetron sputtering in an argon atmosphere with the additions of oxygen and nitrogen. It is shown that the type of substrate influences the surface morphology, with films on silicon being characterized by a more uniform and fine-grained structure. Elemental analysis confirmed the presence of Ti, O, and N and their uniform distribution over the surface of the films. The analysis of the optical spectra showed that the obtained films have a predominantly amorphous structure and are similar in their properties to the composition of $TiO_{1.27}N_{0.49}$, which is consistent with the literature data. The estimation of the band gap yielded values comparable to the published results for titanium oxynitride and titanium dioxide films. The measured electrical resistivity values are in good agreement with the known data and are closer to the characteristics of titanium nitride than titanium dioxide. This confirms the intermediate character of the electrophysical properties of titanium oxynitride between the oxide and nitride phases. The scientific novelty of the work lies in the production of TiO_xN_γ films with reproducible optical and electrical properties using a gas mixture similar in composition to atmospheric air.

The practical significance of the results is related to the possibility of using the obtained films in memristor structures. The prospects for further research include optimizing the composition of films and studying their memristive characteristics.

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