Phase composition investigation of titanium oxide nanostructures obtained by the local anodic oxidation

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Abstract. The paper presents the results of a phase composition study of titanium oxide nanostructures obtained by local anodic oxidation. A mathematical model was presented, which made it possible to calculate the distribution of oxide phases in the nanostructure volume. The results of the X-ray photoelectron spectroscopy (XPS) spectrum analysis are presented, which are consistent with theoretical calculations.

1. Introduction
Modern nanoelectronics development is closely related to the application of new methods for the formation of nanostructures [1-12]. An important task is the controlled formation of nanostructures with specified geometric and physical parameters. This problem is especially relevant for the formation of memristor structures in manufacturing RRAM resistive memory elements, since their characteristics are affected not only by the geometric dimensions, but also by the distribution of the phase composition in the oxide nanostructure (ONS) volume, which is the basis for the memristor manufacturing. One of the promising methods for the formation of forming-free memristor structures based on titanium oxide is local anodic oxidation, which allows the precise fabrication of ONS [13-23]. Nevertheless, existing models of the local anodic oxidation process can only predict the geometric parameters of the formed oxide nanoscale structures [24-26], while the oxide phase composition calculation is not presented in the literature. Therefore, this work aims at investigation of the phase composition distribution in the titanium ONS volume obtained by the local anodic oxidation nanolithography.

2. Theoretical model
ONS formation by the local anodic oxidation method is a multi-stage process including the oxygen ions generation in moist air due to the water molecules decomposition under the external electric field influence and oxygen ions mass transfer from the air to the oxide volume and to the metal-oxide boundary. Therefore, oxide volume increases during metal oxidation (Fig. 1). In addition, it is necessary to consider and calculate the metal oxide phase transitions rate by supplying an additional oxidizing agent to the oxide formed volume. For this, the Ti–O phase diagram was calculated, which showed that with an increase in the oxygen fraction, titanium sequentially oxidized to the TiO, Ti2O3, and TiO2 phases (Fig. 2). Accordingly, when developing a mathematical model, it is necessary to consider the features of each of these processes separately and their influence on the process of ONS formation.
Thus, to solve the problem, it is necessary to solve the system of differential equations:

\[
\begin{align*}
\nabla (\varepsilon \varepsilon_0 \nabla \varphi) &= -\rho(N), \\
\nabla (-\mu \nabla \varphi + D \nabla N) &= R(\varphi),
\end{align*}
\]

(1)

where \( \varphi \) and \( N \) are the electric potential and oxygen ions distribution in the oxide volume, \( \varepsilon \varepsilon_0 \) is the dielectric constant of the medium, \( \rho(N) \) is the oxygen ions volume charge density, \( \mu \) and \( D \) are the oxygen ions mobility and diffusion coefficient, and \( R(\varphi) \) is the rate of oxygen ions generation in the air.

A joint solution of the presented system of equations will allow obtaining the oxygen ions distribution in the oxide volume and the oxygen ions flow to the surface. In addition, thanks to the results obtained, it is possible to calculate the phase transition rate \( \text{Ti} \rightarrow \text{TiO} \rightarrow \text{Ti}_2\text{O}_3 \rightarrow \text{TiO}_2 \).

3. Experimental
To carry out experimental studies on a titanium film about 20 nm thick, formed by magnetron sputtering on a multifunctional Auto 500 installation (BOC Edwards, England), a titanium ONS with lateral dimensions of 300x300 \( \mu \text{m}^2 \) and a height of 4.5 nm was obtained using the probe nanolaboratory Ntegra

![Figure 1. Oxygen ions generation and movement in the oxide volume.](image1)

![Figure 2. Phase diagram of Ti-O system.](image2)
(NT-MDT, Russia) by multiplication of $50 \times 50 \, \mu m^2$ area. The phase composition was studied by X-ray photoelectron spectroscopy (XPS) using a combined spectrometer for quantitative imaging and surface analysis of ESCALAB 250 (Thermo Scientific, USA) with monochromatizing of X-ray AlKα-line. For XPS analysis of the phase composition of the experimental sample in depth, ion profiling was used.

4. Results and discussion

Based on the developed model, the local anodic oxidation process of titanium film was numerically simulated using the MATLAB application package with the Partial differential equation module algorithms, which made it possible to solve nonlinear partial differential equations systems. For this, the electrochemical cell geometry was considered, including AFM probe, air medium, oxide, and metal film, for which a solution to a given differential equations system was found. Then, the distribution of the oxygen ions flow over the metal surface and the oxide growth rate were determined, and phase transitions in the oxide volume were calculated.

As a result, the distributions of the TiO, Ti$_2$O$_3$, and TiO$_2$ phases were obtained (Fig. 3), which showed that the TiO phase was formed near the oxide-metal interface, the Ti$_2$O$_3$ phase was in the oxide bulk, and the TiO$_2$ phase was present near the oxide surface. The results can be explained by the fact that in the local anodic oxidation process, oxygen ions diffuse through the oxide layer to the metal surface and, accordingly, the ion concentration decreases from the air to the metal. Thus, under oxygen deficiency conditions, the TiO phase is formed, and under increased oxygen concentration conditions, the oxide is transformed to TiO$_2$.

XPS analysis of the titanium oxide memristor nanostructure before and after ion etching showed the presence of Ti2p spectra of the core levels of elements (Fig. 4). The phase composition of the titanium ONS uppermost layer corresponds to titanium oxide TiO$_2$. Most likely, this degree of oxidation was obtained naturally under the influence of atmospheric oxygen. Deep profiling of ONS showed that the phase composition of Ti oxide contained three components. Energy of components 458.4, 456.6, and 454.8 eV corresponds to the intermediate oxidation states of TiO$_2$, Ti$_2$O$_3$, and TiO.

![Figure 3. Titanium oxide phases concentration distribution in the O volume.](image-url)
Figure 4. XPS spectra of ONS titanium obtained: (a) on the surface; (b) after etching time of 30 s; (c) after etching time of 60 s; (d) after etching time of 120 s.

Figure 5. Ti oxide phases distribution content in depth.
From the data presented in Figure 4, it follows that with increasing depth of XPS analysis, the content of the Ti$_2$O$_3$ and TiO phases increases exponentially, while TiO$_2$ decreases according to the same exponential law (Fig. 5). So, with an etching time of 120 seconds, the fraction of the TiO$_2$ phase is 3.6 units, the Ti$_2$O$_3$ phase – 13.9 units, and TiO phases – 5.4 units.

The experimental results obtained are in good agreement with the data of mathematical modelling.

5. Conclusion
In this work, we developed a mathematical model that allowed simulating the formation of titanium oxide nanostructures obtained by local anodic oxidation, as well as calculating the distribution of titanium oxide phase composition. Theoretical results correlate with experimental data of the X-ray photoelectron spectroscopy spectrum of titanium oxide nanoscale structures obtained by the local anodic oxidation method.

The obtained results can be used in the development of technological processes for the fabrication of the RRAM element base based on titanium oxide nanostructures.

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