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## Study and production of thin-film memristors based on $\text{TiO}_2 - \text{TiO}_x$ layers

To cite this article: E V Zhidik *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **498** 012022

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# Study and production of thin-film memristors based on $\text{TiO}_2$ – $\text{TiO}_x$ layers

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**Abstract.** Results of production of thin-film memristor MIM-structures based on the stoichiometric ( $\text{TiO}_2$ ) and nonstoichiometric ( $\text{TiO}_x$ ) titanium oxides and contacts without precious and rare-earth metals are given. It is shown that such memristor structures without precious metals show its operability only after the process of electrical forming.

## 1. Introduction

In the sphere of information technology, one of the prior directions is creation of new generation computers, neuronets and artificial intelligence [1]. Resistive random-access memory (RRAM) with a longer time of data storage and higher data density, better in more than dozens of times than any existing type of memory, is considered as the best candidate for computer memory of the future generation.

The structure of switching and memory elements in RRAM represents the system of metal-insulator-metal and the characteristics of this system depend on the composition and structure of the insulating layer. Such structures were predicted in 1971 by L.O. Chua [2] and were called memristors, due to that two stable switching states, high resistance or high conductivity, can be realized in them. The practical realization of memristor-type memory was produced in 2008 by Hewlett-Packard Company [2].

In the Russian Federation, studies concerned with the creation of memristors are conducted in National Research Center “Kurchatov Institute”, Southern Federal University, Voronezh State Technical University, National Research Nuclear University MEPhI, as well as National Research University of Electronic Technology MIET.

So, numerous studies of memristors conducted by Hrapovitskaya et al. [4] showed that properties of such elements are determined by their architecture and materials. Eliseev [5] described the method of the production of memristors based on titanium dioxide ( $\text{TiO}_2$ ). Hrapovitskaya et al. studied the insulating layers of  $\text{TiO}_2$  –  $\text{TiO}_x$ . In the paper [6], the insulator was made as a layer of  $\text{Ti}_{0.85}\text{–Al}_{0.15}\text{–O}$ , and in the paper from Hewlett-Packard Company [7], the insulator was made of 4 kinds of materials:  $\text{TaO}_x$ – $\text{TiO}_{2x}$ ;  $\text{TaO}_x$ ;  $\text{TiO}_{2x}$ – $\text{TiO}_{2x}$ ; and  $\text{TiO}_{2x}$ – $\text{TaO}_x$ – $\text{TiO}_{2x}$  with platinum electrodes.

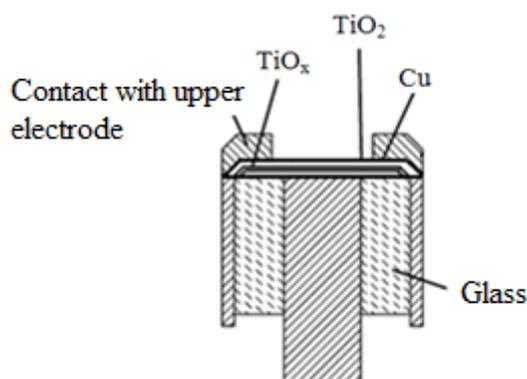
The mentioned studies show that the development of memristors follows the line of the most effective architecture. Besides, the majority of the studies are concerned with the application of the  $\text{TiO}_2$  thin films or  $\text{TiO}_2$ – $\text{TiO}_x$  structure, where  $\text{TiO}_x$  is non-stoichiometric titanium dioxide. At the same time, studies concerned with the impact of the electrode material on the properties of the memristor are very rare.



This paper is concerned with the impact of the material of the memristor electrode on the characteristics of the memristor.

## 2. Results and discussion

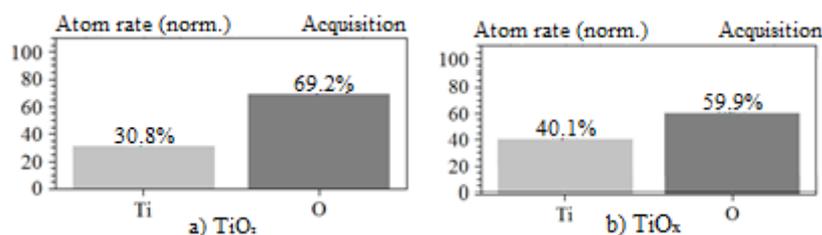
The experimental memristor Mo–TiO<sub>x</sub>–TiO<sub>2</sub>–Cu structure was formed on the surface of a coaxial glass-metal kern. The central molybdenum electrode of the Kern was one of the electrodes of the structure (Figure 1).



**Figure 1.** Schematic picture of memristor structures on the kern-type substrates [3].

TiO<sub>x</sub> thin films with the thickness of 50 nm were obtained by means of magnetron sputtering of titanium target in the gas mixture of Ar (65 %) and O<sub>2</sub> (35 %). At the pressure of  $7 \cdot 10^{-2}$  Torr discharge current was 300 mA and the rate of the thin films growth was 16 nm/min. TiO<sub>2</sub> thin films were obtained by means of magnetron sputtering of the titanium target in the presence of Ar with O<sub>2</sub> (10%) with sputtering process conditions identical to TiO<sub>x</sub>. The rate of growth of TiO<sub>2</sub> thin films was approximately 24 nm per minute.

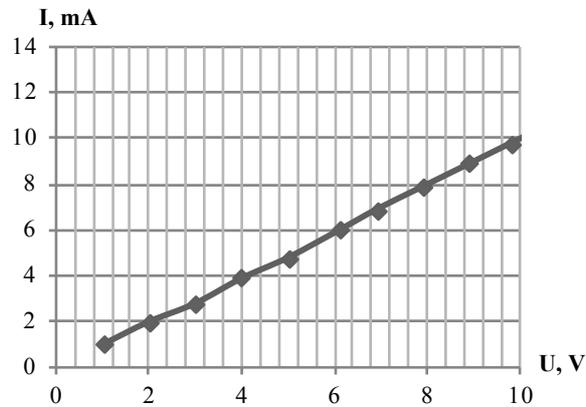
X-ray structural microanalysis was made to control structure of insulating films. It showed that titanium in the obtained thin films had oxidation levels close to that of TiO<sub>2</sub> and Ti<sub>2</sub>O<sub>3</sub>, which was essential for production of memristor structures.



**Figure 2.** Structure of obtained insulating films.

Films of the upper electrode were obtained by means of thermal evaporation of Cu in vacuum with the pressure of  $4 \cdot 10^{-5}$  Torr. The thickness of the film of the upper electrode was 30 nm. The upper electrode was covered by a thick layer of Al outside the center of the kern (Figure 1) for the better electrical contact.

Volt-ampere characteristics were measured in the prepared Mo–TiO<sub>x</sub>–TiO<sub>2</sub>–Cu structures in normal and reversed polarity at atmospheric pressure. Figure 2 shows the averaged volt-ampere characteristic of Mo–TiO<sub>x</sub>–TiO<sub>2</sub>–Cu structures.

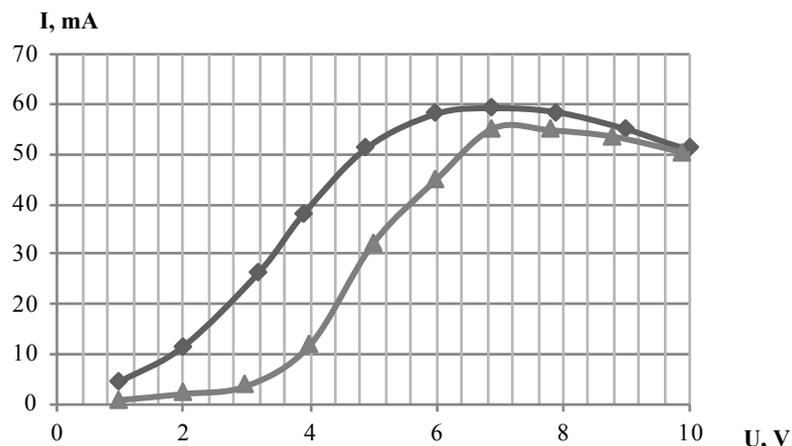


**Figure 3.** Volt-ampere characteristic of Mo-TiO<sub>2</sub>-TiO<sub>2</sub>-Cu structure at the atmospheric pressure.

The measured volt-ampere characteristic monotonically increases without a region of negative differential resistance, which means that there are no switching states of low-resistance and high-resistance. The absence of the region of negative differential resistance can be explained by the insufficient work function of electrons from Cu, which is approximately 4.34 eV. At the same time, the work function for materials used for the production of memristors such as TiO<sub>2</sub>, Au, and Pt is 4.7 eV, 5.1 eV and 5.32 eV, respectively.

The electrical forming process of the Mo-TiO<sub>2</sub>-TiO<sub>2</sub>-Cu structure, which was described in detail in [10], allows the compensation of the disadvantage mentioned above.

The samples with Mo-TiO<sub>2</sub>-TiO<sub>2</sub>-Cu structure were placed in the vacuum at the pressure of 10<sup>-3</sup> Torr. Electrical forming was conducted by a bias supply of 10 V, the exposition time of 10 minutes at the reversed polarity. Changes in the volt-ampere characteristic after the process of electrical forming are shown in Figure. 4



**Figure 4.** Volt-ampere characteristics of states with different conductivity:

- ◆ -low-resistance state;
- ▲ -high-resistance state.

In order to detect the hysteresis of the structure, the voltage was gradually increased on the structure until the value of 10 V. After that, the voltage was gradually decreased, which corresponds to the high-resistance state.

The measured volt-ampere characteristics point to that initially, the Mo–TiO<sub>x</sub>–TiO<sub>2</sub>–Cu structure does not show switching properties of memristors, but after the electrical forming of the obtained structures in vacuum its volt-ampere characteristics reveal the region of negative differential resistance.

### 3. Conclusion

The conducted study of memristor structures shows that structures without precious metals (such as the Mo–TiO<sub>x</sub>–TiO<sub>2</sub>–Cu structure) are operable only after the electrical forming in vacuum. During the electrical forming, the irreversible changes occur in the MIM-structure, which lead to the appearance of the regions with negative differential resistance in the volt-ampere characteristic.

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