Obtaining memristor elements based on non-noble materials

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Abstract. This study is aimed at creating memristor elements based on TiO_2/TiO_x layers with electrodes that do not contain noble and rare-earth metals, by vacuum deposition method. The characteristics of these elements analyzed by voltammetric methods show that the appearance of an *N*-type region of negative differential resistance on the current–voltage curve can be caused only by metal electrodes whose vacuum work function exceeds that of TiO_2. The appearance of the *N*-type region on the current–voltage curve of a memristor element is possible only after electrically assisted vacuum forming. Mo–TiO_2/TiO_x –Ni/Cu structures, for which the I_{LR}/I_{HR} ratio reaches two orders of magnitude at a voltage of less than 4 V, have the most stable parameters.

Introduction

In the 21st century, there is a trend towards the active development of new hardware implementations of analog neurochips with frequency modulation based on hybridization of CMOS (complementary metal-oxide-semiconductor) technology and memristors — passive elements that are able to change their resistance depending on a charge flowing through it [1]. This implementation paradigm for artificial neural networks makes it possible to copy the brain structure with high accuracy. In this structure, neurons are made of transistors, while synapses are replaced by memristors. Due to this architecture, functioning mechanisms of living neurons can be reproduced much more accurately than DC digital or analog implementations [2].

The following analogy between this type of artificial neural networks and living neurons can be drawn. The synaptic transmission speed depends on activation time of neurons: the shorter the time interval between activations is, the faster the signal is transmitted through a synapse. The memristor array works exactly in the same way: when the current is applied at intervals of 20 ms, the memristor resistance is half that at intervals of 40 ms [3].

The memristor was developed and described by Leon Chua in 1971 [4]. Chua was deeply convinced that there was a fourth device that could ensure a conceptual symmetry with a resistor, inductor and capacitor.

Chua's ideas were brought to life by Hewlett-Packard employees when in 2008 Williams announced the discovery of a memristor based on a nanoscale thin film of titanium dioxide [5]. The development of memristor elements makes it possible to

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implement an “authentic” neural network in practice, while the physical properties of memristors allow them to be reduced up to ten nanometers and scaled up for mass production.

Despite some extensive studies of memristor elements that have been completed to date, e.g. in [5–8], most of them concern the application of TiO_2 films or a TiO_2/TiO_x structure, where TiO_x is non-stoichiometric titanium dioxide. The electrodes in these elements are made of only noble metals — Pt or Au.

This study is aimed at creating and studying characteristics of memristor MDM (metal-dielectric-metal) elements based on TiO_2/TiO_x layers with electrodes that do not contain noble or rare-earth metals.

Experiment

The influence of the upper electrode material on switching properties of memristors was analyzed on the basis of Mo–TiO_2/TiO_x–Ni, Mo–TiO_2/TiO_x–Cu, and Mo–TiO_2/TiO_x–Ni/Cu structures. Core-type structures were used as a substrate [9] (Fig. 1).

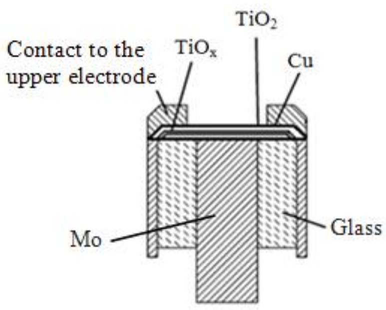

Fig. 1. A schematic representation of the MDM element based on a core-type substrate.

In order to produce the test memristor elements, 50-nm TiO_2 films were deposited by magnetron sputtering of a titanium target in Ar with 35% O_2 and at a gas mixture pressure of $7 \cdot 10^{-2}$ mm Hg. The discharge current was 300 mA, which corresponded to a film deposition rate of 16 nm/min [9]. TiO_x films were deposited by magnetron sputtering of the Ti target in Ar with 10% O_2 under equal identical conditions. The approximate growth rate of the TiO_x film is 24 nm/min.

In order to check the composition of dielectric films, an X-ray diffraction microanalysis was carried out (Fig. 2). The results show that, in terms of oxidation degree, titanium in the produced films is close to TiO_2 and Ti_2O_3 compounds that are necessary for obtaining memristor elements.

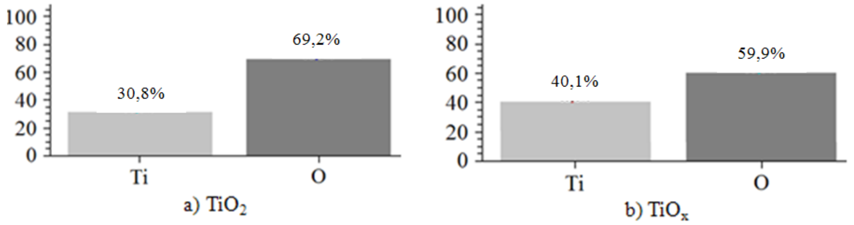

Fig. 2. Composition of the produced dielectric films (atomic percent).

Films of the upper electrode were deposited by thermal evaporation of Ni and Cu in vacuum at a pressure of $2 \cdot 10^{-5}$ mm Hg. A film of the upper electrode is 30 nm thick. For a better contact, a thick metal layer was sputtered onto the upper electrode along the edges of the core so that to avoid covering the working area.

Current–voltage characteristics of the produced MDM elements were measured at a constant voltage in both straight and reverse polarity. The measured current–voltage characteristics show an ohmic linear behavior, without an *N*-type region of negative differential resistance. Apparently, the absence of this region is associated with the insufficient work function of electrons from Cu and Ni, which is 4.34 eV and 4.48 eV, respectively. For materials used as memristor electrodes, this parameter should be no less than the work function of electrons from TiO_2 (4.7 eV) [10]. For example, the work function of electrons from Au and Pt, metals that are traditionally used for memristor contacts, is equal to 5.1 eV and 5.32 eV, respectively. This disadvantage can be compensated for by subjecting the MDM element to the electrically assisted forming procedure described in detail in [11].

To carry out the forming procedure, samples were exposed to vacuum at a pressure of 10^{-2} mm Hg. The forming procedure was conducted at a voltage of 14 V. Mo–TiO_2/TiO_x–Ni/Cu structures were formed almost instantaneously. Mo–TiO_2/TiO_x–Ni structures were formed during 30 minutes. For a shorter forming time, the current–voltage characteristics did not change their pattern. An interesting result was obtained after the deposition of a 20-nm thick copper layer onto Mo–TiO_2/TiO_x–Ni structures. These structures were formed at 14 V during 10 minutes. Then current–voltage characteristics were measured in vacuum, in different states.

Results

The current–voltage characteristics of the produced MDM elements were measured before and after the forming. Before the forming, the current–voltage curve is monotonically increasing, without a region of negative differential resistance (Fig. 3).

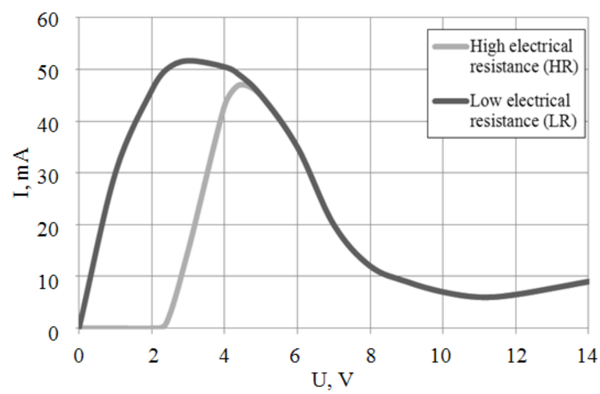

Fig. 3. The current–voltage curve of Mo–TiO_2/TiO_x–Ni/Cu structures with different conductivity values.

The Mo–TiO_2/TiO_x–Ni/Cu structures are formed rapidly and have a shape memory. The I_{LR}/I_{HR} ratio reaches 100 at a voltage of less than 4 V. The current–voltage characteristics of these structures are more stable than those of Mo–TiO_2/TiO_x–Ni, while their switching currents are three orders lower than those in Mo–TiO_2/TiO_x–Cu.

The surface of one of the formed MDM elements is presented in Figure 4.

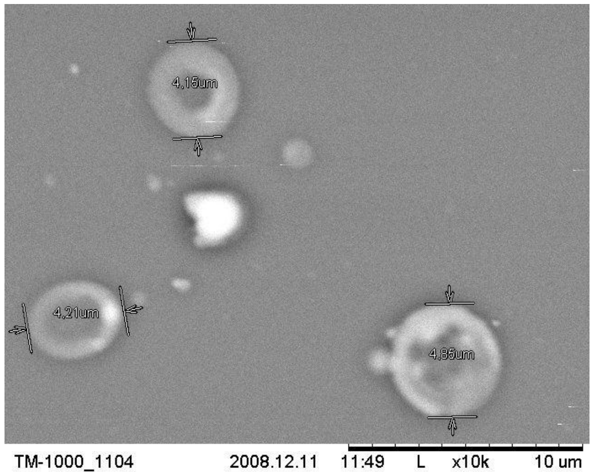

Fig. 4. The surface of the formed MDM structure: Mo–TiO_2/TiO_x–Ni/Cu.

Thus, after the forming process, channels with a diameter of about 4.4 μm are formed on the surface of the MDM structures. The density of these channels is $5 \cdot 10^7$ cm^{-2}. This value is close to the density of the channels obtained in [11].

Conclusion

During the production and research of the memristor elements based on non-noble materials, it was established that these elements could become serviceable only after electrically assisted vacuum forming.

Electrically assisted forming induces some irreversible changes in the test elements that give rise to the *N*-type region of negative differential resistance. At the same time, in the high-resistance state, the currents are reduced by 2–3 orders of magnitude compared to the low-resistance state. It is an acceptable value for a memristor element.

Further research in this area will be aimed at determining a switching mechanism and memory of memristors. As of today, the only proposed switching mechanism is a diffusion of oxygen vacancies from TiO_x to TiO_2 [12]. In our opinion, this switching mechanism is controversial and unproved.

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