Investigation of memristor effect on basis of thin-film oxide dielectrics modified by carbon

Yu V Sakharov
Tomsk State University of Control Systems and Radioelectronics (TUSUR), 40, Lenin Str., Tomsk, Russian Federation

Corresponding author’s e-mail: iurii.v.sakharov@tusur.ru

Abstract. The regularities of the change of electrophysical properties of memristor structures based on porous films of titanium dioxide are considered at their modification by carbon. It is shown that the introduction of impurity results in the significant change of the electrophysical properties of memristor structures based on porous films of titanium dioxide. The purpose of this paper is to reveal the regularities between the electrophysical properties of elements of non-volatile memristor memory and the phenomena of switching and memory at atmospheric pressure.

1. Introduction
To date, the main problem of electronics is to find an alternative to FLASH memory. It relates to electrically reprogrammed semiconductor memory and stores bits in the form of electric charges. The main disadvantage of FLASH memory consists in electrostatic leakages that must be addressed at the transition to microcircuits of the nanometer scale [1]. As a result, all attempts to increase the density of information storage result in the significant shortening of the time of its storage.

The implementation of new perspective memristor elements will allow us to create effective computing systems to fulfill the goals set. A memristor is a passive element of electronics, the key feature of which is the ability to change electrical resistance depending on the value of the electric field applied to the active layer. They possess resistive switching and can remember the conductivity state for a long time because it is stored not in the form of a charge and is consequently completely non-volatile. Resistive switching is the control of the value of electrical resistance of metal-dielectric-metal structures by means of short-term influence by strong electric fields. Non-volatile memory possesses a number of advantages, such as longer period of storage of information and high-density of data recording, significantly exceeding that of existing types of memory.

A memristor has a simple enough structure: a layer of metal oxide, embedded between two metal electrodes, i.e. metal-dielectric-metal structures (MDM). Also, this effect is present in the structures based on semiconductor substrates, i.e. metal-dielectric-semiconductor structures (MDS). The titanium oxide $\text{Ti}_x\text{O}_{2x-1}$ with the thickness of 5-40 nm is the most widely investigated. This memristor effect was observed for the first time on the mentioned type of titanium oxide. Widely investigated are also other metal oxides: $\text{ZrO}_2$, $\text{HfO}_2$, $\text{VO}_2$, $\text{Nb}_2\text{O}_5$, $\text{TaO}_x$, $\text{MoO}_2$, $\text{WO}_3$, $\text{Fe}_2\text{O}_3$, $\text{NiO}$, $\text{Co}_2\text{O}_3$, $\text{Al}_2\text{O}_3$ [2]. Nevertheless, the switching effect differs for different materials. On the basis of the current-voltage characteristics (CVC), the switching effect can be divided into two types: unipolar switching and bipolar switching. The typical CVC for the two types is shown in Fig. 1 [3].
At unipolar switching, the switching depends on the amplitude of applied voltage rather than on polarity (Fig. 1a). The structures are exposed to the forming process, after which they go into a low-resistance state (LRS). After the voltage reset, structures go into a high-resistance state (HRS). The switching from HRS to LRS occurs by the feeding of the threshold voltage that exceeds the voltage of the reset. Such a type of switching is observed in many insulation oxides, for example, in TiO$_2$ [4].

At bipolar switching, the switching depends on the direction of the applied voltage (Fig. 1b). This type of switching is observed in such complex oxides such as Hf$_x$Al$_{1-x}$O$_y$ and TiO$_2$-TiO$_x$ [4, 5].

2. The process of electrical forming

The forming process consists in the following: an MDM structure is placed in a vacuum of no more than 1 Pa and the voltage of some critical value is applied. After a while, some nonreversible changes of electrical properties will occur in the structure; in particular, the conductivity will significantly increase, the structure will obtain a switching effect and a memory effect, and also electroluminescence in visible range, there will occur the electron emission in vacuum, and the CVC will obtain the N-type negative differential resistance. This process is referred to as forming, and the voltage under which the forming occurs is named as a voltage of forming [6].

These changes are connected to the presence of formed channels in the structure. The distinguishing characteristic of the formed channels is the absence of the upper electrode. Immediately after forming, the formed channels have an average diameter of 0.1-1 microns. The channel body is referred to as high conductivity channel; it is filled with microcrystals of the formed dielectric. The upper electrode over the channel is missing. It melts and detaches itself due to local heating and intensive gas emission, and a gap of 10-20 nm (a nanogap) is formed between the electrode edge and the high conductivity channel [6].

3. Experiment and measuring techniques

The experiment was carried out on Al-TiO$_2$-Al and Al-TiO$_2$-Ag structures. The Al films of 100 nm were applied by thermal evaporation in vacuum for use as a bottom electrode. For the counter electrode were used 30 nm films of Al and Ag, applied by thermal evaporation in vacuum. The dielectric was applied by means of magnetron sputtering of the titanium target in an atmosphere of oxygen at the pressure of $4\times10^{-2}$ Pa in a vacuum chamber [7]. The thickness of the dielectric was 30 nm. The modification of the films by carbon was carried out by the sputtering of composite target Ti:C with various area ratios. At the same time, the magnetron construction allowed us to change the area ratio of Ti and carbon on the composite target. The amount of carbon introduced into the TiO$_2$ film was determined using the carbon area on the composite target and expressed in percentages of $S_c$. The modification of the TiO$_2$ film by...
carbon will permit to increase its porosity and to create additional oxygen vacancies, which will accelerate the process of electrical forming and will improve the resistive switching [8].

4. Experiment results and analysis

When applying the voltage of 12 V to an Al-TiO$_2$-Al structure, some nonreversible changes of electrical properties occur, which can be observed in the fact that the steady leakage current increases sharply, and the electroluminescence in the visible range and emissive current appear [9]. The forming time is counted from the moment of the voltage application to the moment of the relative stabilisation of steady leakage current. The dependence of steady leakage current from time is presented in Fig. 2a. The analysis of this dependence allows us to note that the modification of TiO$_2$ film by carbon considerably accelerates the forming process, thus increasing the steady leakage current passing through the structure. The main cause of the steady leakage current growth is the increase in density of the formed channels, which are mainly localised near pores. It is indicated by the electroluminescence pattern and the analysis of the structure surface before and after forming.

After the termination of the forming process, the CVC of both structures have considerably changed: steady leakage currents have significantly increased, and also there appeared a site of the negative differential resistance of N-type (Fig. 2b). Both structures have a hysteresis of current. However, the structures with the modified dielectric have higher $I_{\text{max}}/I_{\text{min}}$ relation.

![Figure 2. The change of steady leakage current in time (a) and CVC after forming (b) for Al-TiO$_2$-Al structures without the modification of the dielectric by carbon $S_c=0\%$ (1) and with the modified dielectric $S_c=60\%$ (2)](image)

A rapid disconnection of voltage from the MDM structure on a site results in the appearance of memory effect. As a result, the structure "remembers" the electrical conductivity at the moment of the disconnection, and a new CVC will have the given electrical conductivity from 0 V to some threshold voltage $U_{\text{th}}$ (3-4 V) or reset voltage (Fig. 3) on the site. This state can be erased by applying a voltage higher than threshold $U_{\text{th}}$ or can be recorded again by applying a voltage $U>U_{\text{min}}$ with subsequent rapid disconnection. Thus, the system takes on two stable states: LRS and HRS. Also, the given states are completely non-volatile and are resistant to moderate heat, light, as well as magnetic fields.

A prominent feature of the forming process is the necessity of a vacuum to fulfil it. Also, all above-mentioned effects can be observed only in a vacuum.

A distinct feature of the Al-TiO$_2$-Al structure with a carbon modified dielectric is the possibility to observe all of these effects in argon at atmospheric pressure when Ag films are used as an upper electrode. Besides, steady leakage currents decrease by a factor of 10-20.
Figure 3. Initial CVC (1) and a memory effect (2) for an Al-TiO$_2$-Al structure with a modified dielectric $S_c=60\%$

5. Conclusion

The modification of TiO$_2$ films by carbon results in the formation of a loose structure of the dielectric, which contains a considerable quantity of pores and gas inclusions [10]. It is supposed that it is the pores that are centres for the localisation of the formed channels, defining all properties of the formed structures. Accordingly, the increase in density of the formed channels results in the increase of steady leakage currents passing through the dielectric.

The reason of these changes consists in the chemical reaction between oxygen and carbon, resulting in the formation of a volatile compound of CO or CO$_2$. The evaporation of this volatile compound from the dielectric film leads to the formation of see-through pores and gas inclusions, and also to the formation of areas of partial titan oxidation. It is supposed that the kinetics of the forming process development can vary in the case of use of a porous dielectric with a higher number of defects.

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