Effect of ion irradiation on resistive switching in metal-oxide memristive nanostructures

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Abstract. The development of artificial intelligence systems is needed to solve many important challenges in neurobiology and neuroengineering for recreation of brain functions and efficient biorobotics. Here we propose a metal-oxide memristive device compatible with CMOS technology and suitable for hardware implementation of neuromorphic tasks. However, metal-oxide memristors have a significant drawback such as variation of resistive switching parameters due to the stochastic nature of filament formation in oxide material. In this work, we control the filament formation process by irradiation of oxide film surface with heavy ions. We have shown that the irradiation of oxide surface in the Au/SiO$_2$/TiN memristive device with Xe$^+$ ions (at energy of 5 keV) decreases the fluctuations of electroforming voltage, current-voltage characteristics during switching and increases the current ratio in the high/low resistance states. The ability to control internal parameters of the memristor can allow more efficiently using memristor as an element of neural networks and other neuromorphic circuits.

1. Introduction
Coupling memristors in the form of resistive switching devices with neurons and design of neuromorphic systems based on them is one of the most promising areas of interdisciplinary research. Research on artificial brain strategies construction has progressed exponentially over the last few decades. It should be noted that the development of neuromorphic electronic systems brought together such disciplines as biology, medicine, computer science, and robotics. Such systems are of special interest for researchers working in the fields of fundamental nonlinear dynamics of complex and multistable systems [1, 2], intellectual adaptive automatic control systems, biorobots and medical applications in devices for monitoring and stimulating the brain activity in the framework of neuroprosthetic tasks [3-5]. In this context, memristive devices have been an object of intensive research in recent years including neuromorphic applications [6-9].

Memristor or “memory resistor” works as a resistor and, at the same time, has a memory effect. As an element of electrical circuits, memristor can be realized in the form of a resistive switching device (RRAM – Resistive Random Access Memory) capable of changing the resistance depending on the magnitude of electric field and / or current [10]. In the case of inorganic solid state memristive device, the resistance changes due to a reversible transformation of atomic structure in the nanometric region of dielectric (oxide) film deposited between two conductive electrodes [11]. The resistive state changed under a particular applied voltage can be stored in a nonvolatile manner, which allows the usage of memristive nanostructures in the RRAM [12] and “logic-in-memory” devices [13]. The
metal-oxide-metal capacitor-type nanostructures (called metal-oxide nanostructures) are formed on a standard silicon substrate, compatible with CMOS technology for designing mixed analog-digital electronic circuits. The local processes responsible for resistive switching provide a high degree of miniaturization, speed and low energy consumption. The ability of memristive device to change the conductivity depending on the electrical stimulation makes it an electronic analog of the synapse – the connection between neurons determining the coupling strengths [14-16].

Nowadays, significant progress has been achieved in using memristors to mimic the properties and functions of biological synapse. Nevertheless, the hardware implementation of brain-like electronic systems based on memristive devices is still at the early stage of development. The widespread application of RRAM memory devices is constrained by the fact that, along with the great advantages of this memory type, it has a significant drawback – a large variation of parameters and low reproducibility. This is due to the peculiarities of the structure and functioning of resistive switching devices. The fact is that the metal-oxide-metal memristive device usually acquires the necessary property of switching from the high-resistance to the low-resistance state and back only after the so-called electroforming, when thin conductive paths (filaments) are formed inside the oxide layer depending on the external voltage of a certain amplitude and polarity. This process is random (stochastic): filaments are formed from nuclei that arise in localized areas of strong electric field at the interface between dielectric and electrode, as a rule. In this case, the roughness of interface, the grain structure of the oxide film, and the fluctuations of its composition play important roles. As a result, the number, shape, and composition of the filaments strongly depend on a number of random factors. Moreover, during the memristor operation, which requires numerous switching cycles, the structure of filaments ensemble may change, which leads to the change or even complete degradation of switching characteristics.

The idea of this work is to control the process of filaments growth by irradiation of the oxide surface (which serves as the metal-oxide interface after the electrode layer deposition) by heavy ions (method of ion implantation). A heavy ion in its motion in a solid displaces atoms from lattice sites and thereby creates a “cloud” of defects – vacancies and interstitial atoms – the so-called displacement cascade [17]. Due to the high concentration of defects, the displacement cascades located in the oxide near the metal electrode have a high conductivity (they are practically equipotential), and it should be expected that some of them will be electrical field concentrators during the electroforming process. The ion irradiation permits to control well the average concentration of defects in cascades, the average length of cascades in the direction of ion beam and in lateral direction, as well as the average distance between cascades. These parameters are strictly determined by the type of ions, their energy and fluence. It can be expected that the role of the above mentioned uncontrolled factors affecting the result of electroforming (filament growth) would decrease and, consequently, the reproducibility of switching parameters would increase.

In this paper, the suggested idea is demonstrated for the Au/SiO₂/TiN memristive structures, in which the SiO₂ thin film is a dielectric layer, and layers of Au and TiN are the top and bottom electrodes, respectively. It should be noted [18] that the SiO₂ thin film as a switching dielectric corresponds well to the condition of compatibility of memristors with existing silicon microelectronics technology, in which SiO₂ is a standard component of MOSFET transistors.

2. Experimental

The Au/SiO₂/TiN memristive structures were fabricated on a thermally oxidized silicon substrate with a magnetron-sputtered conductive TiN layer. Silicon dioxide films (40 nm thick) were deposited by magnetron sputtering of quartz. Ion irradiation was carried out after the deposition of SiO₂ layer. After irradiation, the top Au electrodes with area of $1.2 \times 10^{-3}$ cm² and thickness of 40 nm were deposited through a mask. Ion irradiation was carried out by using the ILU-200 ion implanter. The Xe⁺ ions were chosen for irradiation. The choice of this type of ions has resulted from the fact that their large mass allows creating displacement cascades with a high density of point defects [17]. It is necessary to ensure the high conductivity of defective “clouds” so that they can play the role of
filament nuclei. In addition, the Xe$^+$ ions do not reveal chemical activity, which could have an additional effect.

One of the requirements for the choice of irradiation conditions arising from the above idea is that the ion range must be substantially lower than the oxide film thickness; otherwise, the cascades serving as areas with high conductivity will short out the dielectric. Another requirement is that the cascades should not overlap with each other, which imposes a limitation on the irradiation fluence.

The energy of Xe$^+$ ions was chosen to be 5 keV in connection with these requirements. (Irradiation with energies lower than 5 keV on the ILU-200 is technically difficult). To select the optimal fluence range, we calculated the spatial distribution of vacancies in atomic displacement cascades using the SRIM software [19]. These calculations allowed us to determine the irradiation fluence, at which the cascades are distributed on defined distances from each other. It was established that the maximum lateral radius of the cascade in SiO$_2$ is 4.6 nm, according to a 100-fold decrease in the average concentration of oxygen vacancies within it. The maximum allowable fluence ($9\times10^{12}$ cm$^{-2}$) was defined from the condition that the average distance between the cascades is equal to the lateral diameter of the cascade. At the specified energy, ions generate displacement cascades in the near-surface SiO$_2$ layer with a depth of up to 9 nm. The position of the SRIM-simulated displacement cascades in the SiO$_2$ layer of the memristive structure is shown in Figure 1.

![Figure 1](image_url)

**Figure 1.** Schematic cross-section of a switching layer with displacement cascades used for the filament nucleation. Cascades were simulated by the SRIM code for Xe$^+$ ions with energy of 5 keV.

The Agilent B1500A semiconductor device analyzer was used to measure current-voltage characteristics. The electroforming was performed in the first voltage sweep from zero to some negative values on top electrode (– 5 V), as a result of which the device switches to the low resistance state (LRS). During the subsequent positive voltage sweep, when its value achieves a certain value, the device switches to a high resistance state (HRS). Then, when a negative voltage sweep is applied, a switching occurs to the HRS. These switching is repeated cyclically. We are interested primarily in the variations of voltage required for electroforming, as well as the ratio of resistances in LRS and HRS.

### 3. Results and discussion

Figure 2 shows the current-voltage characteristics of the reference memristive devices and the devices modified by Xe$^+$ ion irradiation for several measurement cycles carried out after electroforming. The current-voltage characteristics are typical of filamentary metal-oxide memristive devices [9-11]. It can be seen that the $I$-$V$ characteristics vary from cycle to cycle due to the stochastic nature of the processes described above.
Figure 2(a, b). Typical I-V characteristics of the SiO$_2$-based memristive devices fabricated without (a) and with (b) the use of Xe$^+$ irradiation with a fluence of 1∙10$^{11}$ cm$^{-2}$.

The average values of minimal voltages needed for electroforming and their device-to-device variation for the reference and ion-modified devices are listed in Table 1 (the averaging was performed over 4 devices). As can be seen in Table 1, the variation of electroforming in the ion-modified devices is much lower than that in the reference devices. As mentioned above, it is assumed that this result is a consequence of a decrease in the degree of randomness at filaments forming: instead of forming on random inhomogeneities of the metal-SiO$_2$ interface, in the modified structures, filaments are formed mainly at the locations of displacement cascades, the concentration of which is strictly determined by the ion fluence.

Table 1. Electroforming voltages for the SiO$_2$-based memristive devices fabricated with and without the use of 5 keV Xe$^+$ irradiation.

| Xe$^+$ fluence, cm$^{-2}$ | Electroforming voltage, V | without irradiation | with irradiation |
|--------------------------|---------------------------|---------------------|------------------|
| 1∙10$^{11}$             |                           | (3.0 ± 1.6)         | (2.9 ± 0.3)      |
| 1∙10$^{12}$             |                           | (3.4 ± 1.3)         | (3.7 ± 0.8)      |
| 1∙10$^{13}$             |                           | (4.2 ± 0.2)         | (3.4 ± 0.1)      |

It is seen in Figure 2 that the degree of cycle-to-cycle variation of I-V characteristics in the irradiated structures is also somewhat lower. But the most pronounced difference in the current-voltage characteristics of irradiated structures from the current-voltage characteristics of structures without irradiation is the difference in current ratio in the two states – LRS and HRS: in irradiated structures, this ratio is substantially higher, which is a positive factor for the operation of memristors as memory elements. The increased resistance ratio is explained by the fact that the filaments formed after irradiation, apparently, have a smaller thickness (arising predominantly on displacement cascades). Due to this, the oxidation process of filament section adjacent to the electrode is facilitated when a positive voltage is applied (such oxidation causes the switching from LRS to HRS [10]), as a result, the resistance in the HRS is increased. Thus, the ion irradiation influences the nucleation of filaments, as well as the operation parameters of the studied memristive devices.

4. Conclusions

To summarize, it has been established that the Xe$^+$ ion irradiation of SiO$_2$ dielectric layer in the Au/SiO$_2$/TiN memristive structure leads to the decrease in variation of electroforming voltages, as well as to the increase in the ratio of currents in the high-resistance and low-resistance states. This indicates that the method of ion implantation is promising to control the internal operating parameters
of memristive devices and for the improvement of a stable operation of memristive devices. We believe that such memristive devices will provide higher efficiency in the imitation of neuromorphic functions.

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