Influence of ion irradiation on the resistive switching parameters of SiO$_x$-based thin-film structures

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Abstract. For the memristive Au/SiO$_x$/TiN/Ti structures produced by magnetron sputtering and demonstrating reproducible bipolar resistive switching, the dependence of resistive states on the dose of irradiation with H$^+$ and Ne$^+$ ions with energy of 150 keV has been established. It is shown that, under proton irradiation, the resistive switching is not deteriorated up to the dose of $1 \times 10^{16}$ cm$^{-2}$, and, in the case of Ne$^+$ irradiation – up to the dose of $3.3 \times 10^{15}$ cm$^{-2}$ (equivalent by the ionization losses). As the Ne$^+$ ions produce three orders of magnitude more elastic collisions than protons (for the same dose), the obtained results allow to predict the high radiation tolerance of the memristive structures to both ionization and displacement damage.

1. Introduction

One of the relevant problems of present electronics is the development of a new generation non-volatile memory (Resistive Random Access Memory – RRAM) based on using two stable states of a material (usually insulator): a high-resistance state (HRS) and a low-resistance state (LRS). Bipolar switching between these states is realized by applying voltage pulses of different polarity. Such a memory device is also called memristor [1] that can be implemented in a simple capacitor-like structure of the “metal-insulator-metal” (MIM) type [2]. Because of the simplicity of fabrication, scalability and low switching time, RRAM devices can replace in the nearest future the entire hierarchy of computer memory.

The development of new radiation-tolerant electronic components is also very important for the space and nuclear power applications. In view of the fact that irradiation leads to the loss of efficiency of traditional charge-storage Flash-memory, RRAM could be one of the main types of memory for the applications in radiation environments. However, the environmental test of radiation tolerance is quite complicated and often not available for researchers. We know only few works where HfO$_2$-based memristors were irradiated by high-energy protons (1-10 MeV) [3,4,5]. The authors of these studies have established that LRS, due to the formation of conductive channels (filaments) in oxide under the electroforming, shows high radiation hardness, and changes, observed in HRS, do not significantly affect the memory properties. However, the observed phenomena may differ for the memristive structures based on other oxide materials. Moreover, the data obtained in different experimental conditions cannot provide sufficient information about the mechanisms of radiation effects for the definite type of memristors.
Previously, we have shown that the tolerance of microstructures, which are located near the surface of solids, to the fast neutron irradiation can be examined by medium-energy ion irradiation [6]. The size of memristor active area in the MIM structure is limited by the thickness of insulator and electrodes and these regions are located at the depths of tens of nanometers. That is why we can successfully apply ion beams with medium energies to simulate the influence of high-energy particles, such as fast neutrons of cosmic protons.

At the present work, H\(^+\) ions (150 keV) were used to simulate the impact of cosmic protons on the parameters of resistive switching (RS) in CMOS-compatible silicon oxide-based MIM-structures. To determine the contributions of both ionization and elastic losses, the MIM-structures were also irradiated by much heavier Ne\(^+\) ions (150 keV).

2. Experimental

The capacitor-like MIM structure was deposited on CMOS-compatible TiN (25 nm) / Ti (25 nm) / SiO\(_2\) (500 nm) / Si substrate. SiO\(_x\) film (40 nm thick) was deposited using RF-magnetron sputtering system MagSputt 3G-2 (Torr International) from fused silica in the argon-oxygen mixture (8% oxygen content) at substrate temperature of 200 °C. The top Au electrodes (40 nm) were deposited by DC-magnetron sputtering at 200 °C. The current-voltage (I-V) characteristics were measured by Agilent B1500A semiconductor device analyzer. The sign of bias on the device corresponds to the potential of top electrode (Au) relative to the grounded bottom electrode (TiN). After electroforming and switching to both HRS and LRS, the fabricated MIM structures were irradiated by H\(^+\) and Ne\(^+\) ions (150 keV) with doses in the range of 1·10\(^{11}\) – 1·10\(^{16}\) cm\(^{-2}\).

3. Results and discussion

In the initial state, the MIM-structure shows typical characteristics of a capacitor with the silicon suboxide as dielectric layer. After electroforming, which was provided at negative bias of about 3-6 V, the current grows by several orders of magnitude. The structure begins to manifest reproducible bipolar resistive switching (RS) with the switching bias of 3-4 V and large number of switching cycles (more than 10\(^4\)) [7]. The typical RS hysteresis loops for the Au/SiO\(_x\)(40 nm)/TiN/Ti structures subjected to electroforming are given in figure 1.

![Figure 1. I-V characteristics of the Au/SiO\(_x\)/TiN structure. Schematic representation of the structure cross-section is shown on the inset.](image-url)
To choose irradiation regimes for the present MIM-structure, the elastic and ionization losses under irradiation with 150 keV hydrogen ions and 10 MeV space protons, and also for 150 keV neon ions were calculated using the SRIM software [8] (figure 2). The figure shows that the elastic and ionization losses in SiO$_x$ film under 10 MeV proton irradiation are almost 14 times lower than under irradiation with 150 keV H$^+$ ions. Elastic losses (a number of displacements/vacancies) for 150 keV proton irradiation are about three order of magnitude lower than for Ne$^+$ ions of the same energy.

![Figure 2. Depth distribution of ion energy ionization losses (a) and generated in elastic collision vacancies (b) calculated by SRIM [8].](image)

Radiation tolerance of memristors may depend on the state in which they were under irradiation. Therefore, ion irradiation was performed for the structures which were before irradiation in each state – HRS and LRS. The values of the LRS and HRS currents measured at +0.5 V vs. the dose of H$^+$ and Ne$^+$ irradiation are given in figure 3. Experiments were carried in the following manner. Before the irradiation, the structures were switched into HRS or LRS with the subsequent current measurement at the reading voltage, after that they were irradiated to a certain dose and again subjected to switching and measurement (5 switching cycles) and so on (the accumulated doses are indicated in figure 3).
In the vast majority of cycles, there has been no significant change in currents for proton irradiation up to the maximal used dose \((1 \cdot 10^{16} \text{ cm}^{-2})\) independently of the structure state before irradiation. Since the RS in investigated structures is maintained after proton irradiation up to the dose of \(1 \cdot 10^{16} \text{ cm}^{-2}\) (figure 3), then one can conclude that the RS will be maintained under irradiation by cosmic protons with the doses much higher than maximal dose used in this work. In the case of Ne⁺ irradiation, the situation is similar for currents in the HRS up to the maximal dose \((3.3 \cdot 10^{15} \text{ cm}^{-2})\). Note that for the used doses, the integrated values of energies spent on the ionization losses near the surface are equal for both types of used ions. At the same time, when the memristor is irradiated in HRS, there can be a spontaneous switching to LRS during irradiation with both types of ions, however the HRS is always reset after the subsequent switching cycle. The nature of spontaneous resistive switching under irradiation requires further investigation: it may be due to high energy ionization losses (i.e., charge accumulation) and possible elastic collisions of ions with atoms of oxide (formation of recoils and the corresponding radiation defects that is more significant for Ne⁺ ions). In the case of Ne⁺ irradiation, some noticeable degradation in the HRS (decrease in resistance) is observed for the highest dose, probably due to the accumulation of radiation defects in the entire volume of oxide material.

![Figure 3](image_url)

**Figure 3.** Currents measured in HRS and LRS of Au/SiOₓ/TiN/Ti structures without irradiation and after irradiation with H⁺ \((a)\) and Ne⁺ \((b)\) vs. the number of switching cycles after each irradiation. Arrows show the increased currents measured after irradiation.
The nature of the observed reproducible bipolar RS in SiO$_x$-based thin-film memristive structures can be related to the formation and local oxidation of silicon conducting channels (filaments) in the bulk of SiO$_x$ layer [9]. Such filaments produced by breaking Si-O bonds under high electric stress can not be affected by ion irradiation in LRS, whereas the local dielectric interlayer formed in the site of filament oxidation can be sensitive to both ionizing and defect-producing irradiation, which leads to some observed HRS changes.

4. Conclusions
In summary, the irradiation with medium-energy H$^+$ and Ne$^+$ ions has revealed high stability of resistive states of Au/SiO$_x$/TiN/Ti memristive structures. The obtained results allow to predict the high radiation tolerance of the SiO$_x$-based memristors to both ionizing irradiation and displacement damage.

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References
[1] Chua L 1971 IEEE Transactions on Circuit Theory CT18 507
[2] Strukov D, Snider G, Stewart D and Williams R 2008 Nature 453 80
[3] Lee D, Lee J, Jung S, Kim S, Park J, Biju K P, Choe M, Lee T and Hwang H 2011 IEEE Transactions on Nuclear Science 58 3317
[4] Butcher B, He X, Huang M, Wang Y, Liu Q, Lv H, Liu M and Wang W 2010 Nanotechnology 21 475206
[5] Bi J S, Han Z S, Zhang E X, McCurdy M W, Reed R A, Schrimpf R D, Fleetwood D M, Alles M L, Weller R A, Linten D, Jurczak M and Fantini A 2013 IEEE Transactions on Nuclear Science 60 4540
[6] Tetelbaum D I, Guseinov D V, Vasiliev V K, Mikhaylov A N, Belov A I, Korolev D S, Obolensky S V and Kachemtsev A N 2014 Nucl. Instr. Meth. Phys. Res. B 326 41
[7] Mikhaylov A N, Belov A I, Guseinov D V, Korolev D S, Antonov I N, Efimovych D V, Tikhov S V, Kasatkin A P, Gorshkov O N, Tetelbaum D I, Gryaznov E G and Yatmanov A P 2015 Mat. Sci. Eng. B 194 48
[8] Ziegler J F, Ziegler M D and Biersack J P 2010 Nucl. Instr. Meth. Phys. Res. B. 268 1818
[9] Mehonic A, Cueff S, Wojdak M, Hudziak S, Jambois O, Labbe C, Garrido B, Rizk R and Kenyon A 2012 Journal of Applied Physics 111 074507