The effect of plasma immersion ion implantation of Ne\(^+\) or Ar\(^+\) or Kr\(^+\) on the forming voltage of the resistive switching in the structure Ni/Pt/HfO\(_2\)(10nm)/TaN(5nm)/TiN

O O Permyakova\(^1,2\), A V Miakonkich\(^1\), K V Rudenko\(^1\), A E Rogozhin\(^1\)
\(^1\)Laboratory of Microstructuring and Submicron Devices, Valiev Institute of Physics and Technology RAS, Moscow 117218, Russia
\(^2\)Department of Physical and Quantum Electronics, Moscow Institute of Physics and Technology (State University), Dolgoprudny 141701, Russia

o.permyakova@phystech.edu

Abstract. The effect of ion implantation on the characteristics of resistive switching in the structure of Ni/Pt/HfO\(_2\)/TaN/TiN with an oxide layer thickness of 10 nm is considered. It was shown that after implantation of Ne\(^+\) ions, the forming voltage decreases by 0.5 V, while after implantation of Ar\(^+\) ions, the share of the forming-free cells increased from 0.1 to 0.6. Resistive switching after implantation of Kr\(^+\) ions is entirely absent.

1. Introduction
In this paper, we consider the effect of plasma immersion ion implantation on the characteristics of resistive switching. Devices with the property of resistive switching are called memristors. Generally, a memristor has at least two different resistance states: low resistance state (LRS) and high resistance state (HRS). The listed property makes it possible to use the memristor as an element of the non-volatile memory – ReRAM (resistive random-access memory). The main advantages of such memory are its simple structure, low power consumption, high speed and scalability, and compatibility with the current technological processes of microelectronics [1].

Despite the simplicity of manufacturing a ReRAM element, a forming process is usually required to activate the resistive switching, which requires significantly higher voltages than the voltage necessary to switch between states, also during the forming process there is a sharp shift in the electric current passing through the device, by several orders of magnitude [2]. Often, this process is compared with a soft breakdown of the dielectric [3]. It is possible to develop a structure that does not require forming process or to reduce the forming voltage, for this, methods such as optimization of the structure [4], setting the direction of grain boundary growth in the dielectric [5], ion implantation [6] and annealing [7] are used.

Earlier, a study [8] was conducted for the Al\(_2\)O\(_3\)/HfO\(_2\)/Al\(_2\)O\(_3\)/TiN structure with He\(^+\) ion implantation, which showed a slight reduction in the forming voltage after implantation, but at the same time degradation of other structural parameters. The forming voltage reduction is associated with minor destruction of the oxide structure. As a result, initial defect density involved in the formation of the resistive switching in the dielectric layer increases. It is known that the presence of an Al\(_2\)O\(_3\) layer in the memristor increases the stability of the switching characteristics [9], but at the same time, the forming voltage of the structure and the switching voltage increase. Therefore, an alumina-free
structure was selected. It appears that the resistive switching occurs at the oxide and the active electrode interface due to the incorporation of oxygen ions into the active electrode under the influence of an external electric field. A decrease in the characteristic stresses of the memristor structure is associated with the oxygen affinity of the active electrode material [2]. Therefore, the memristor structure Ni/Pt/HfO$_2$(10nm)/TaN(5nm)/TiN was chosen as the initial one.

2. Experiment
The HfO$_2$(10nm)/TaN(5nm)/TiN structure used in this work was formed on a silicon substrate using the method of plasma enhanced atomic layer deposition. So, a layer of hafnium oxide was deposited using a TEMAH precursor and oxygen plasma at a temperature of 300°C and a pressure of 15 mTorr. A layer of TaN using TBTDET precursor and hydrogen plasma at the same temperature and pressure. Ne$^+$, Ar$^+$, or Kr$^+$ ions with an energy of 5 keV and a dose of $10^{12}$ cm$^{-2}$ were implanted into some structures. Then, using a magnetron sputtering, an upper Ni/Pt electrode was deposited. The area of top electrodes was $0.02$ mm$^2$.

The current-voltage characteristics were measured using Keithley 4200-SCS for ten cells of each structure. Each showed structure was measured at least one hundred cycles within voltage interval from -1.0 V to 1.0 V and current compliance for the SET process 0.01 A.

3. Result and discussion
The I – V characteristics of the initial structure (Figure 1) show low switching voltages in the range of -1 − 1 V (Table 1). High currents of $10^3$ − $10^2$ A and the repeatability between switching cycles are also visible. One of ten structures did not require forming process and the average forming voltage was 2.3 V. To reduce the forming voltage, immersion ion implantation was used before the creation of the upper electrode since the implantation of Ne$^+$ ions did not change the number of the forming-free cells, while the forming voltage decreased up to 1.7 V. Implantation of heavier ions allowed to increase the number of structures that do not require an electroforming process. After Ar$^+$ implantation, six out of ten structures did not require the electroforming process. On the other hand, the average forming voltage increased to 2.5 V. The implantation of Kr$^+$ ions led to a hard breakdown of the dielectric because resistive switching either was not observed at all or was observed during a small number of cycles.

Table 1. Mean voltages of structures.

|                      | Forming voltage, V | SET voltage, V | RESET voltage, V | Forming-free$^*$ |
|----------------------|-------------------|----------------|------------------|-----------------|
| Initial              | -2.3 ± 1.0        | 0.71 ± 0.07    | -0.90 ± 0.09     | 0.1             |
| Ion implantation of Ne$^+$ | -1.7 ± 1.0       | 0.80 ± 0.10    | -0.84 ± 0.05     | 0.1             |
| Ion implantation of Ar$^+$ | -2.5 ± 0.9        | 0.81 ± 0.14    | -0.89 ± 0.07     | 0.6             |

$^*$part of cells not requiring forming process

Ion implantation affects not only the forming voltage, but also the dispersion of the switching characteristics. So as the ion mass increases, the dispersion of the low-resistance switching voltages (V$_{SET}$) also increases (Table 1). The dispersion of characteristics for different cells of the same structure can be seen when comparing the cumulative functions for resistances (Figure 2) at a voltage of -0.1 V. For the initial structure, the window between the HRS and LRS values for different cells of the structure is visible. In contrast, after implantation, such a window disappears. Besides, an increase in the dispersion of resistances is noticeable. An increase in the standard deviation of the resistive switching characteristics can be associated with the formation of multiple conductive filaments.
Figure 1. I–V characteristics of the resistive switching of the initial structure Ni/Pt/HfO$_2$/TaN/TiN.

Figure 2. Plots of cumulative functions for ten cells of each structure: a) initial structure, b) structure after ion implantation of Ne$^+$ ions and c) structure after ion implantation of Ar$^+$ ions; The solid line shows the resistance in the high resistance state at a voltage of -0.1 V, the dashed line shows the resistance in the low resistance state at -0.1 V, the dashed-dotted line shows the median resistance value in this state.

4. Conclusion
The HfO$_2$/TaN/TiN structure has a high variability of characteristics from cycle to cycle and low switching voltages. Plasma-immersion ion implantation can reduce the electroforming voltage of resistive switching or, when implanting heavier ions, increase the number of cells that do not need an electroforming process.

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