The effect of ion implantation and annealing on forming process in Al₂O₃/HfO₂/Al₂O₃ memristor structure

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Abstract. In this paper, we study the effect of annealing and plasma immersion ion implantation of He⁺ conditions on forming voltage for the Al₂O₃/HfO₂/Al₂O₃ memristive structures. Planar memristor structures were obtained by PEALD. It was shown that He⁺ implantation and annealing lead to decrease of forming voltage but also increase the dispersion of the set voltage of the memristive structures.

1. Introduction
One of the most prominent types of the next-generation non-volatile memory is resistive switching memory (ReRAM). It has the following advantages: high-speed operation, low power consumption, comparatively simple structure and amazing scalability. Typically, ReRAM cell has metal-insulator-metal (MIM) structure, different materials from metal oxides to various organic compounds can act as insulators.

The main property of ReRAM cells is the ability to switch between two stable resistance states: high resistance state (HRS) and low resistance state (LRS). Switching between these states is accomplished by applying voltage: V_SET to switch from HRS to LRS (SET process) and V_RESET to switch from LRS to HRS (RESET process). One of the hypotheses explains the possibility of resistance switching in the oxide based structures as the formation of a conductive filament (CF) between metal electrodes that consists of oxygen vacancies. Therefore, the first action before measuring the characteristics of the memristor structure is the formation of such a filament upon a electroforming voltage (V_FORMING). During this process, the current in the structure increases abruptly, that causes problems of using structures in nano- and microelectronics due to large current. Hence, it is important to either reduce the forming voltages or create forming-free structures [1, 2]. It was shown that the Al₂O₃/HfO₂/Al₂O₃ stack-based structure demonstrates the properties required in ReRAM [3].

Several ways to improve the ReRAM structure characteristics by incorporation of defects were proposed. For instance, annealing in different media (vacuum, oxygen, inert gases) [4] and temperature [5] or focused ion beam processing [6] were suggested. In this paper we present the investigation of the effect of post-metal annealing in nitrogen atmosphere and pre-metal He⁺ ion implantation on the forming voltage for the Al₂O₃/HfO₂/Al₂O₃ structure.
2. Experiment
The Al₂O₃(6nm)/HfO₂(10nm)/Al₂O₃(3nm) structures were formed by plasma enhanced atomic layer deposition (PEALD) on the Si wafers covered by sputtered TiN. After that structures were coated Pt (10 nm) and Ni (50 nm) through the shadow mask. Then some of the structures were annealed in the nitrogen atmosphere at 450°C for 300 s. For other samples pre-metal plasma immersion ion implantation of He⁺ was used to incorporate defects in the dielectric stack structure. The energy of He⁺ ions was 2 keV. The dose value was $10^{16}$ cm⁻². After implantation some structures were annealed. Planar structure with common electrode were investigated (fig. 1).

Current-voltage characteristics were measured using semiconductor characterization system Keithley 4200-SCS and Micromanipulator probe station. Each showed structure was measured at least one hundred cycles with a 2.5 V stop voltage and a current compliance for the SET process 1 mA. The electrode area was measure with an interference microscope Zygo NW5000. The areas of the top electrodes were $2.01 \pm 0.03 \times 10^4 \mu$m² for the initial structure (fig. 2), $1.67 \pm 0.02 \times 10^4 \mu$m² for the structure annealed in an atmosphere of nitrogen, and $3.48 \pm 0.03 \times 10^4 \mu$m² for the structure after ion implantation.

3. Result and discussion
For each type of structure (initial, annealed in a nitrogen atmosphere, after plasma immersion ion implantation), up to 20 devices were formed. The main parameters for these devices are presented in the Table 1. The smallest forming stress is achieved for the structures after ion implantation, but at the same time for the structures the yield is lower. This means that more devices irreversibly breakdown through the forming process. Simultaneously, that forming voltage includes in dispersion of forming voltage for structure annealed in nitrogen atmosphere. Besides structures have showed similar RESET voltages.

|                     | Forming voltage, V | SET voltage, V | RESET voltage, V | Yield |
|---------------------|--------------------|----------------|------------------|-------|
| Initial             | $13.1 \pm 0.8$     | $-2.3 \pm 0.3$ | $1.5 \pm 0.3$    | 0.88  |
| Nitrogen atmosphere | $10.9 \pm 0.6$     | $-2.1 \pm 0.5$ | $1.5 \pm 0.2$    | 0.72  |
| Ion implantation    | $10.6 \pm 0.2$     | $-4.0 \pm 0.9$ | $1.4 \pm 0.3$    | 0.74  |

The following figures (fig.3-5) show values for the HRS and LRS at a voltage of -0.1 V for 100 cycles, with a stop voltage of 2.5 V. Apparently, a high variance for both states, and therefore high
variability from cycle to cycle for a single cell, but this behavior is typical for the first hundred cycles, as indicated in the article [2]. Memristor structure after ion implantation has not the finest characteristics, such as RESET voltage and yield, among the presented structures (table 1) including cycle-to-cycle variability (fig.5). There are also problems with switching between resistance states.

Figure 3. Resistance state of initial structure. Blue circle – low resistance states (LRS), red square – high resistance states (HRS).

Figure 4. Resistance state of annealed structure in nitrogen atmosphere. Blue circle – LRS, red square – HRS.

Figure 5. Resistance state of structure after ion implantation with dose $10^{16}$ cm$^{-2}$. Blue circle – LRS, red square – HRS.

Figure 6. Current-voltage characteristics. Red solid line – initial structure, blue dashed line – structure annealed in nitrogen atmosphere.

The hysteresis of the initial structure (fig. 3) decreases after a one hundred cycles, however, with increasing stop voltage the hysteresis increases again. But reference structure has a resistance ratio of less than ten, which is necessary for applications. Post-processing of the structure allows to increase the resistance ratio, consequently after annealing, the value of the high resistance slightly decreases, while the low resistance decreases almost by an order of magnitude, which makes it possible to
increase the resistance ratio. However, from the figure 6 it can be seen that in the structure cycle-to-cycle variability is not the best. For some devices the ratio of resistance lowered after the post-annealing. Besides, there are two types of hysteresis, that seems to be associated with different types of conductivity, it is clearly seen for the hysteresis of the initial cell, that can be associated with a CF that is not fully formed due to a significant change in resistance in the LRS and a change in slope (type of conduction) voltage-current characteristics.

Figures 7 and 8 showed conventional view of the cycle-to-cycle variability in the current-voltage characteristics. It seems, that the annealed structure has larger hysteresis, but greater variation in SET voltage, but on average their values are close to 1.5 V (Fig.9).

Basically, there is no spread of RESET voltage in the main and the cumulative functions. That allows us to say that post-processing mainly affects the formation of the conductive filament and its properties.

**Figure 7.** Current-voltage cycle-to-cycle variability characteristic of initial structure.  

**Figure 8.** Current-voltage cycle-to-cycle variability characteristic for structure annealed in nitrogen atmosphere.

**Figure 9.** Cumulative function of switch voltages. SET voltages in the left and RESET voltages in the right. '+' - structures annealed in nitrogen atmosphere; 'x' – initial structures.
4. Conclusion
The effect of annealing and plasma immersion ion implantation of He\(^+\) conditions on forming voltage for the Al\(_2\)O\(_3\)/HfO\(_2\)/Al\(_2\)O\(_3\) memristive structures was studied. Planar memristor structures were obtained by PEALD. We have investigated how post-processing influence the forming voltage and further functioning of the structures. It appeared that forming voltage decreases after post-processing. In the case of ion implantation structures have large cycle-to-cycle variability and in the case of annealing structures have larger range of SET voltages. In the same time, average RESET voltage is the same for measured memristor structures.

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