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Low resistance state degradation during endurance measurements in HfO_2/HfO_XN_Y-based structures

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The mechanism of resistive switching in Pt/HfO_2(8 nm)/HfO_XN_Y(4 nm)/TiN structures, in which there are two resistive switching modes: bipolar resistive switching and complementary resistive switching. We demonstrate that resistive switching without external current compliance is possible. It is shown experimentally that the conductivity in the low-resistance state corresponds to the space-charge-limited current. A qualitative model is proposed that describes the transition from bipolar resistive switching to complementary resistive switching using Schottky barrier modulation at the metal-insulator interface. Based on this model, an explanation is given for the degradation of the low-resistance state during endurance measurements.

Keywords: memristor, hafnium oxide, complementary resistive switching, bipolar resistive switching, endurance.

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1. Introduction

Modern memory devices have reached the scale limit due to tunneling effects and leakage currents through defects in the dielectric. And this means that new types of memory are needed. One of the promising devices is RRAM (resistive random access memory) due to the estimated retention for more than 10 years, high switching speed, as well as the possibility of integration into a crossbar array [1]. In addition to the usae as a memory device, RRAM can be used as a grid of analog synapses for neuromorphic systems with energy consumption comparable to the energy consumption of a biological synapse [2].

The element of RRAM is a memristor — metal-insulator-metal (MIM) structure. The switching between the high-resistance state (HRS) and low-resistance state (LRS) of the device takes place when the memristor operates. Resistive switching (RS) occurs due to the breaking and recovery of the conductive filament. The conductive filament is formed from oxygen vacancies in memristors with anionic switching type, for example, memristors based on transition metal oxides [3]. Electroforming is necessary to form a conductive filament in a dielectric. During electroforming, oxygen vacancies are formed due to redox reactions at the boundary with a chemically active electrode with a high affinity for oxygen. The electrode is called inert in this work if there is no oxygen exchange near it.

RS is called bipolar RS (BRS) if the high-resistance and low-resistance states are clearly distinguishable at low voltages on the $I-V$ characteristics, and switching from a low-resistance to a high-resistance state and back occurs at different voltage polarities. RS in memristors with one active layer is called complementary RS (CRS) if the resistance states are indistinguishable at low voltages. It is possible to resolve one of the main problems of the crossbar array using CRS — sneak path issue [4]. For the first time, CRS was proposed for two anti-serially connected memristors with BRS, recently the possibility of CRS in memristors with one active layer based on hafnium oxide was shown: HfO_X [5], $HfAlO_X$ [6].

The main problems of memristors are the non-reproducibility of RS characteristics and the low endurance. In this paper, the endurance is the number of resistive switching cycles before the high-resistance and low-resistance states of the memristor cease to be distinguishable. Despite the fact that memristors with a high endurance, more than 10^{11} switching cycles were shown, these data are usually given for single devices [7]. The degradation of the resistance value in the low-resistance state [8] is often noted. Understanding the degradation processes of the resistance value in the low-resistance state is important to increase the reliability of the RS memristor.

The process of resistive switching of memristors based on hafnium oxide was investigated in this paper, and the relationship between a decrease in the enduarnce and the transition from BRS to CRS was demonstrated. An asymmetric structure Pt/HfO_2(8nm)/HfO_XN_Y(4nm)/TiN was formed by plasma-enhanced atomic layer deposition to investigate this connection. This paper presents studies of individual devices of the structure with rapid degradation of the resistance value of the low-resistance state to the resistance value of the high-resistance state. It was shown by a study of the mechanisms of conductivity in the low-resistance state, that the decrease in the memristor rewriting resource and the transition from BRS to CRS are associated with the recombination of positively charged oxygen vacancies with oxygen ions at the boundary with a chemically active electrode.

2. Experiment procedure

The structure Pt/HfO_2(8nm)/HfO_XN_Y(4nm)/TiN was formed by plasma-enchanced atomic layer deposition. TEMAH (Tetrakis(ethylmethylamino)hafnium) and water vapor or hydrogen plasma, respectively, were used as precursors for HfO_2 and HfO_XN_Y. The structure was formed at a temperature of 350°C. The upper electrodes were formed by magnetron sputtering of platinum through a shadow mask. The area of the upper electrode was $0.0360 \pm 0.0015\,\mathrm{mm}^2$.

The $I-V$ characteristics were measured using a 4205-PG2 pulse generator and a 4200-SCP2 digital oscilloscope integrated into the Keithley 4200-SCS. During all measurements, the common lower electrode was grounded. During quasi-static measurements, pulses with a duration of $5 \cdot 10^{-7}$ s were supplied from -2.0 to 2.5 V increments of 0.1 V. The enduarance of the memristor was measured using pulses of constant amplitude -2.0 V when switching to a low resistance state, 2.5 V when switching to a high resistance state and 0.4 V when reading the resistance value, the duration of each pulse was $5 \cdot 10^{-7}$ s.

3. Experimental results and discussion

For the formation of a conductive filament in the structure under study, electroforming is necessary, the average electroforming voltage was -7.7 V. Figure 1 shows the $I-V$ characteristics for the BRS and for resistive switching after degradation of the resistance value of the low-resistance state, which is similar to the CRS. Typical switching voltages before the endurance test were -0.83 ± 0.9 and 0.89 ± 0.5 V for switching to the low-resistance and high-resistance states, respectively.

The plot of the endurance is shown in Figure 2. The gradual degradation of the resistance value of the low-resistance state begins with 170 the switching cycle, and for the first time the resistance states become indistinguishable at the 500th cycle of RS. Not all devices of the studied structure degraded so quickly, but in this work the mechanism of endurance degradation was investigated, therefore this element of the structure was considered.

An analysis of the conductivity mechanisms in the low-resistance state which differ visibly during the transition from one type of resistive switching to another (Figure 1) was carried out to study the processes of resistive switching and endurance degradation in the structure of Pt/HfO_2(8 nm)/HfO_XN_Y(4 nm)/TiN. As a result of the analysis of the conduction mechanisms, we determined that the main low-resistance conduction mechanism for both modes of resistive switching is a space-charge-limited current (SCLC).

The mechanism of conductivity was studied with negative voltage In the low-resistance state for eliminating the impact of the switching process to a high-resistance state. A transition from the SCLC current mechanism in the mode of empty traps ($I \propto V^{3.45}$) [9] to the SCLC current with fully occupied traps ($I \propto V^{1.98}$) was detected for the CRS without current compliance (Figure 3) [10]. The linear dependence of the current logarithm of on the

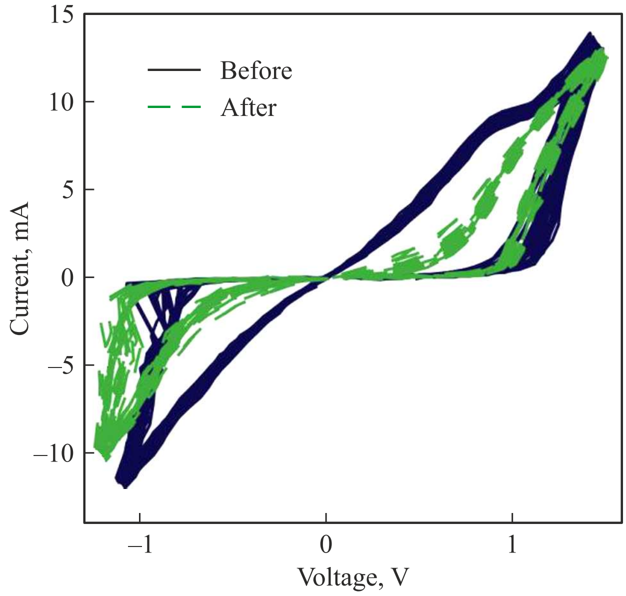

Figure 1. $I-V$ charcteristics of Pt HfO_2(8 nm)/HfO_XN_Y(4 nm)/TiN structure.

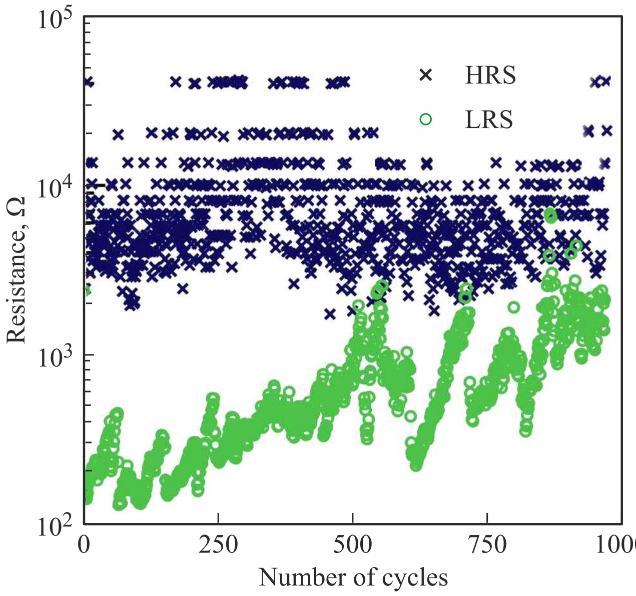

Figure 2. Endurance measurement of the Pt HfO_2(8 nm)/HfO_XN_Y(4 nm)/TiN structure with rapid degradation of the resistance value in the low-resistance state. Blue cross — resistance value in the high-resistance state, green circle — resistance value in the low-resistance state. (A color version of the figure is provided in the online version of the paper).

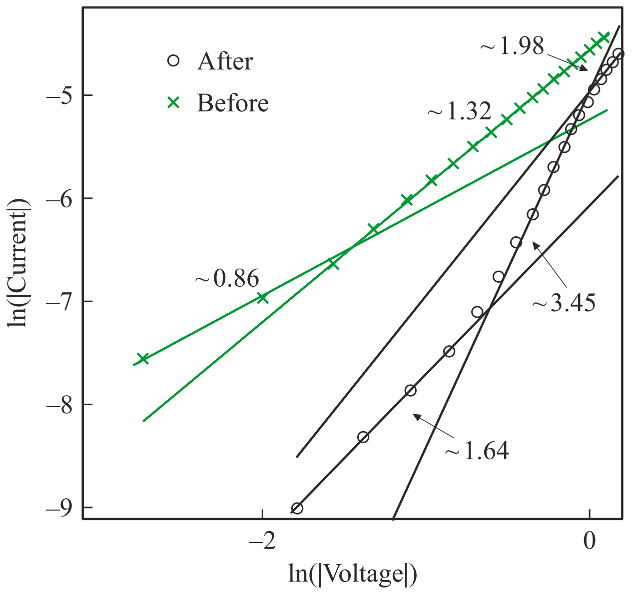

Figure 3. Study of low-resistance conductivity for the Pt/HfO_2(8 nm)/HfO_XN_Y(4 nm)/TiN structure.

voltage logarithm observed with low voltage SCLC was not observed due to the error of pulse measurements at currents less than 70 μA. In BRS, a linear dependence is also observed on a double logarithmic scale, but the slope of the curve ~ 1.32 does not correspond to the SCLC. Approximation of such a dependence using SCLC is possible if we assume the presence of a Schottky barrier at the cathode [11]. Thus, CRS is observed at a minimum value of the Schottky barrier height or its absence, and BRS — in the presence of a Schottky barrier at the cathode. Additional study is needed to specify the value of the Schottky barrier at which the transition between the two RS modes occurs.

We assume that the change in the height of the barrier at the metal-insulator boundary occurs due to a change in the concentration of positively charged vacancies near the [12] boundary. This effect is similar to an increase in the Schottky barrier at the metal-semiconductor interface with an increase in the concentration of the acceptor impurity in the semiconductor [13]. Thus, the increase in the value of the Schottky barrier height is associated with such a position of the quasi-Fermi level at which vacancies near the boundary are positively charged [14]. In this case, a gradual increase in the resistance value in the low-resistance state is associated with a decrease in the number of positive vacancies near the boundary with the active electrode. The initial structure was formed asymmetrically, with fewer vacancies near the HfO_2/Pt boundary, and the emergence of new ones is unlikely due to their high energy of formation at this boundary [14]. A decrease in the number of positively charged vacancies near the boundary TiN/HfO_XN_Y can occur in two main ways: 1) due to recombination of oxygen vacancies with oxygen ions at the active electrode (TiN); 2) due to migration of positively 2+ charged vacancies to the opposite boundary HfO_2/Pt. The first option is most likely due to the gradual depletion of the memristor endurance (Figure 2). Previously, the dependence of the memristor switching mechanism on the thickness of the oxygen exchange layer for memristors based on HfO_2, Ta_2O_5 [15] was experimentally shown. CRS was observed with complete oxidation of the oxygen exchange layer at a thickness of 5 nm, and BRS — at an oxygen exchange layer thickness of > 15 nm. The authors find using simulation that the transition from BRS to CRS is determined by the asymmetry of the output at the electrodes. However, the description of the reduction of the endurance within this model is more complicated when considering a single structure, since it is necessary to show a change in the operation of the electrode output during the operation of the memristor.

4. Conclusion

The transition from BRS to CRS is investigated in this paper using the analysis of conduction mechanisms. The degradation of the resistance value in the low-resistance state was analyzed. It was experimentally shown that the conductivity in the low-resistance state at CRS is determined by the SCLC. In case of BRS, the conductivity of the low-resistance state is also determined by the SCLC, but with a rectifying contact, which occurs due to the accumulation of positively charged vacancies near the active electrode. Based on the constructed model, it is concluded that the endurance degradation the memristor structure occurs due to the recombination of positively charged oxygen vacancies with oxygen ions at the boundary with the active electrode.

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Conflict of interest

The authors declare that they have no conflict of interest.

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