Resistive switching in the Au/Zr/ZrO$_2$–Y$_2$O$_3$/TiN/Ti memristive devices deposited by magnetron sputtering

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Abstract. Bipolar resistive switching phenomenon in the Au/Zr/ZrO$_2$–Y$_2$O$_3$/TiN/Ti memristive devices deposited by magnetron sputtering has been studied. The structure of devices and electrical measurements data for the temperature range from 77 to 490 K are analyzed. The stable switching is demonstrated at room temperature, but the decrease in the resistive switching performance at elevated temperatures is observed.

1. Introduction
The effects of memristive (resistive) switching and memory in the metal–insulator–metal (MIM) devices have been studied extensively in recent years because of the fundamental interest to the structural and electrical phenomena taking place in memristive nanostructures as well as of the potential applications of these phenomena. The nonvolatile memory of new generation – Resistive Random Access Memory (ReRAM) is one of such applications [1-3].

Due to the ability to change the resistance continuously subject to applied voltage (analogously to the biological synapse), the memristive devices are considered now as the basic elements of artificial neural networks of new generation designed to imitate the adaptive behavior of living systems [4, 5]. Transition metal oxides are considered now to be the most promising dielectric layer materials from the technological viewpoint. The bipolar resistive switching (RS) in these oxides is currently attributed to the formation and destruction of conductive filaments as a result of reduction/oxidation (redox) electrochemical reactions under the application of electric bias.

Zirconium oxide (ZrO$_2$) is one of the most extensively studied oxide materials for the memristive devices [2, 3], since it is well compatible with the modern complimentary-symmetry metal-oxide-semiconductor (CMOS) integrated circuit technology. It is worth noting that the application of yttria-stabilized zirconia ZrO$_2$–Y$_2$O$_3$ (YSZ) along with the stabilized hafnia in the memristive devices has the following advantages. The change of stabilizing oxide (Y$_2$O$_3$ in the case of YSZ) fraction allows tailoring the concentration of oxygen vacancies, which determines their mobility, the rate of redox reactions responsible for the electric field distribution in a dielectric film and their electric conductivity, which, in turn, determines the RS parameters.

The goal of the present work was to investigate the elementary processes responsible for the bipolar RS in the Au/Zr/YSZ/TiN/Ti memristive devices prepared by magnetron sputtering compatible with the modern Si-based CMOS technology. The data of structural investigation and electrical measurements for the memristive devices in the temperature range of 77 ÷ 490 K are discussed.
2. Materials and Methods

The Au/Zr/YSZ/TiN/Ti devices were deposited by magnetron sputtering using the Torr International® MagSputTM 3G2 and 2G1-1G2-EB4-TH1 vacuum thin-film deposition systems on the SiO$_2$/Si substrates. The YSZ layers (12 mol.% of Y$_2$O$_3$) were deposited by radio-frequency (RF) magnetron sputtering at the substrate temperature of 300°C. The Au top electrodes with the area of $8.2 \times 10^{-3}$ cm$^2$ were deposited by direct-current (DC) magnetron sputtering. The intermediate Zr layer was introduced between the YSZ film and top Au electrode to improve the adhesion of Au to YSZ and to reduce the work function of the top electrode material. The nominal layer thicknesses were 500 nm for SiO$_2$, 25 nm for Ti, 25 nm for TiN, 40 nm for YSZ, 3 nm for Zr, and 40 nm for Au.

The structural investigation was carried out by high-resolution cross-sectional transmission electron microscopy (XTEM) using the Jeol® JEM-2100F microscope operated at acceleration voltage of 200 kV (a part of shared research facilities of Research and Educational Center for Physics of Solid State Nanostructures at Lobachevsky University). Such electrical parameters of the memristive devices as the current-voltage ($I$–$V$) characteristics within the temperature range $T = 77$ ÷ 490 K and the admittance were measured using the Agilent® B1500A semiconductor device analyzer. Particularly, the frequency dependencies of the differential capacitance $C_{p(s)}$ and conductance $G_{p(s)}$ of the memristive devices in the parallel (p) and serial (s) equivalent circuits of a capacitor [6] at zero voltage bias were measured in the frequency range $f = 10^3$ ÷ $10^6$ Hz. Then, the frequency dependencies of the resistance $R_{p(s)}$ were derived from the measured data. The endurance characteristics were measured by reading current values at $+0.5$ V between the 120 ms write and erase pulses with amplitudes of $+5$ and $-5$ V, respectively. The voltage bias was applied to the top electrode. The measurements were carried out in air ambient unless otherwise specified.

3. Results and Discussion

The XTEM images of a memristive device are presented in Figure 1. The YSZ film is polycrystalline (similar to the literature data [7]). It is worth noting that the interface of the YSZ film with top metal electrode is rough that originates from the polycrystalline nature of the YSZ film.

![Figure 1. XTEM images of the memristive device.](image)

Typical $I$–$V$ curves of the studied memristive device measured at room temperature are shown in Figure 2. The curves corresponds to the forming process and the bipolar RS from the low-resistive (“ON”) state to the high-resistive (“OFF”) state and back to the “ON” state.
The electron work function is 4.05 eV for Zr, 5.1 eV for Au [8], and 4.5 eV for TiN [9]. Therefore, the intermediate Zr layer reduces the electron work function of the top electrode material essentially. Since the electron work function of Zr is lower than that of TiN, the electron injection from the top electrode into YSZ should be more intensive than that from the base electrode at the same voltage bias. Therefore, the forming (without the current compliance) was performed at negative voltage bias. As a result of forming, the memristive device is switched to the “ON” state. The subsequent application of a positive voltage bias switches the device into the “OFF” state. The corresponding RESET process takes place at $V = V_{\text{reset}}$. The reverse switching from the “OFF” state to the “ON” state takes place at a SET voltage bias $V_{\text{set}} < 0$. Thus, the bipolar RS in the devices under study is of the type classified in [10] as a “counter figure of eight”.

![Figure 2](image)

**Figure 2.** The $I$–$V$ curves of the memristive device measured at $T = 300$ K and voltage sweep rate $\mu = 1.4$ V/s.

In order to clarify the conduction mechanisms in YSZ in the “ON” and “OFF” states, the $I$–$V$ curves presented in Figure 2 are plotted in Figure 3 in double logarithmic scales. These dependencies demonstrate the same slope equal to $\approx 1.0$ at both $V < 0$ and $V > 0$ in the low-voltage range. In the high voltage range, the slope of curves increases up to $1.9$ in the “OFF” state and up to $2.1$ in the “ON” state. The transition between the low-voltage and high-voltage ranges takes place at nearly the same voltage values at $V < 0$ and $V > 0$ (at $|V| \approx 0.7$ V in the “OFF” state and at $|V| \approx 1.1$ V in the “ON” state). So far, the conductivity of the memristive device appears to be the ohmic one in the low-voltage range for both voltage polarities. However, the conduction mechanism changes with increasing the voltage magnitude, and the $I$–$V$ curves take the form of $I \sim V^n$ with $n \approx 2$ pointing to the space charge limited current (SCLC) conduction mechanism [11]. Thus, the SET process is preceded by trapping of electrons at the trap sites in YSZ associated with the T and C centers [12], whereas the RESET process leaves the traps empty.

The admittance measurements [6, 13] at zero voltage bias are used to determine the values of dielectric constant ($\varepsilon_1$, $\varepsilon_2$) of a dielectric layer determined from the capacitance of the memristive devices measured in the parallel capacitor equivalent circuit, as well as the dielectric losses angle tangent ($\tan\delta_1$, $\tan\delta_2$) and the resistances ($R_{p1}$, $R_{p2}$, $R_{s1}$, $R_{s2}$). Here, the index 1 denotes the measurement frequency $f = 1$ kHz and the index 2 corresponds to $f = 100$ kHz. The parameters of parallel equivalent scheme are determined by the electronic phenomena in YSZ, while the parameters featuring the serial equivalent scheme are determined by the resistance of metal electrodes and the one of the transition layer between the metal contacts and YSZ film. The values of these parameters for the studied memristive devices in the initial state as well as in the “ON” and “OFF” states at room temperature are given in Table 1.
The data presented in Table 1 demonstrate that the measured values of dielectric constant for YSZ coincide approximately with the values reported in the literature [14]. This means that the electrode resistance in the studied devices is low enough. Note that the values of dielectric constant of the YSZ films almost don’t change when the transition comes from the initial state to the “ON” state that evidences the formation of filaments in the YSZ films during forming, which determines the high dielectric losses. The values of dielectric losses in the “ON” state decrease by almost two orders of magnitude with increasing the measurement frequency from 1 kHz up to 100 kHz that can be related to the hopping conductivity in the conductive filaments.

![Figure 3](image)

**Figure 3.** The $I–V$ curves of the memristive device in the “ON” and “OFF” states (Figure 2) plotted in double logarithmic scales.

**Table 1.** The electrical parameters of the memristive devices in the initial state, in the “ON” state, and in the “OFF” state obtained by admittance measurements in the parallel and serial capacitor equivalent circuits.

| State | $\varepsilon_1$ | $\varepsilon_2$ | $\text{tg} \delta_1$ | $\text{tg} \delta_2$ | $R_{p1} (\Omega)$ | $R_{p2} (\Omega)$ | $R_{s1} (\Omega)$ | $R_{s2} (\Omega)$ |
|-------|----------------|----------------|---------------------|---------------------|------------------|------------------|------------------|------------------|
| initial | 23 | 22 | 2.64·10^{-2} | 8.87·10^{-2} | 1.46·10^6 | 4.58·10^3 | 1.02·10^4 | 35.8 |
| ON | 21 | 19 | 70.0 | 8.21·10^1 | 611 | 552 | 611 | 222 |
| OFF | 22 | 21 | 3.47·10^{-1} | 9.09·10^{-2} | 1.13·10^5 | 4.53·10^3 | 1.21·10^4 | 37.1 |

According to the XTEM data, the roughness of the YSZ film interface with the top Au/Zr electrode correlates with the grain boundaries in the oxide film and is greater than that of the base TiN electrode. The top interface inhomogeneities can play a role of electric field concentrators, which favor the formation of filaments during the forming process at negative voltage bias applied to the top electrode. A relatively low electron work function of Zr intermediate layer material ($\approx$ 4.05 eV) also favors the growth of filaments from the top interface. Besides, one should take into account that the electron affinity of YSZ is $\approx$ 2.65 eV [14]. Therefore, the $\alpha$-band lying $\approx$ 1.5 eV below the conduction band edge in YSZ [12] is $\approx$ 4.15 eV below the vacuum level, i.e. below the Fermi level in Zr. This means, that electrons from Zr can be injected into the $\alpha$-band of YSZ in the thermodynamic equilibrium that should favor the formation of conductive filaments at negative voltage bias applied to the top electrode. It should be noted that along with the preferential formation of the filaments at negative voltage bias, the SET process taking place at negative voltage bias occurs at lower voltage magnitude as compared to the RESET process (see Figure 2).

Figure 4 shows a dependence of the current through the Au/Zr/YSZ/TiN/Ti memristive device in the “ON” and “OFF” states at room temperature on the number of pulse-driven switching cycles. As it
follows from Figure 4, the memristive devices demonstrate a high switching endurance. The ratio of the resistances in the “OFF” and “ON” states $R_{ON}/R_{OFF}$ doesn’t change essentially after $10^3$ switching cycles. The variation of the current through the memristor device in the “ON” and “OFF” states is determined by the stochastic nature of the filament formation and destruction. It is worth noting that the switching between the “ON” and “OFF” states is preserved for the duration of voltage pulses as low as 100 ns, what is important for the fast write/erase operation of memory devices.

![Figure 4](image)

**Figure 4.** The dependence of current through the memristive device in the “ON” and “OFF” states at room temperature on the number of the pulse-driven switching cycles.

It is worth noting that the RS phenomenon in the investigated Au/Zr/YSZ/TiN/Ti memristive devices depends weakly on the ambient (vacuum, air) unlike the analogous SiO$_x$-based devices [15]. In particular, the character of $I–V$ hysteresis almost doesn’t change when the memristive device is measured at room temperature in ambient air, in low vacuum ($3-5\times10^{-2}$ Torr), and after letting the ambient air back in the vacuum chamber.

The temperature stability of the RS parameters was studied by measuring the cyclic $I–V$ curves at the temperatures in the range $T = 77 \div 490$ K (Figure 5).

![Figure 5](image)

**Figure 5.** The $I–V$ curves of the memristive device measured at various temperatures. The voltage sweep rate $u = 3.0$ V/s.

The switching voltages $V_{set}$ and $V_{reset}$ in the studied devices depend on the measurement temperature and fall into the ranges $-2.5 \div -5.0$ V and $+3.5 \div +5.0$ V, respectively (see Figure 5). The
resistive switching performance decreases with increasing temperature starting from about 313 K: the values of current through the memristive device in the “ON” and “OFF” states become closer to each other, i.e. the $R_{\text{OFF}}/R_{\text{ON}}$ ratio decreases at all values of the voltage $V$ considered. It is important to note that the increase in current through the memristive device in the “OFF” state with increasing temperature obeys the Arrhenius law: $I(T) \sim \exp(-E_a/kT)$, where $k$ is the Boltzmann’s constant and $E_a$ is the activation energy. The value of $E_a$ at $T > 313$ K obtained from the $I(T)$ dependencies measured at $V = +0.5$ V is $\approx 80$ meV. The mechanism of the observed degradation of the bipolar RS performance in the Au/Zr/YSZ/TiN/Ti memristive devices with increasing the temperature is not clear at the moment and requires further investigation.

4. Conclusion
It can be concluded from the present study that the bipolar RS in the studied Au/Zr/YSZ/TiN/Ti devices originates from the formation and destruction of conductive filaments. According to the XTEM data, the inhomogeneities of the YSZ film interface with the top Au/Zr electrode can act as electric field concentrators, which favor the growth of filaments during the forming process at negative voltage bias applied to the top electrode. A relatively low electron work function of Zr intermediate layer also favors the electron injection in YSZ from the top electrode. The decrease of dielectric losses in the “ON” state with increasing measurement frequency evidences the hopping mechanism of the filament conductivity. However, the conduction mechanism changes to the SCLC at the increased voltage magnitude due to the participation of YSZ defect traps in the electron transport. The bipolar RS in the studied devices is found to be affected weakly by the ambient (air, vacuum) that originates from the fact that the oxygen vacancy concentration in YSZ is determined by the $Y_2O_3$ molar fraction and, therefore, independent of the oxygen content in the ambient. This is an important advantage of YSZ as a material for the memristive devices as compared to other oxides. The YSZ-based MIM nanostructures fabricated by magnetron sputtering demonstrate high enough endurance, fast switching and are promising for the ReRAM applications.

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