Resonant activation of resistive switching in ZrO$_2$(Y) films

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Abstract. Local resistive switching (RS) in ZrO$_2$(Y) films on conductive substrates has been studied using Conductive Atomic Force Microscopy (CAFM). Switching was performed by triangle voltage pulses with superimposed a high-frequency (HF) sinusoidal signal applied to the contact of the CAFM probe to the ZrO$_2$(Y) film (together constituting a nanometer-sized virtual memristor). Earlier, the enhancement of the RS performance has been observed when the HF signal was superimposed onto the switching pulses. The effect was attributed to the resonant activation of the migration of oxygen ions via oxygen vacancies by an external alternating electric field. In the present study, this assumption was confirmed by measuring the frequency dependence of the difference between the probe currents in the low-resistance and high-resistance states with a maximum at about 5 kHz. This frequency corresponds to the characteristic one of the jumps of oxygen ions onto adjacent oxygen vacancies in ZrO$_2$(Y) at 300 K. The experimental results were compared with the results of simulation based on the Chua model of an ideal memristor.

1. Introduction

In recent years, the investigations of resistive switching (RS) have attracted much attention [1]. RS consists in bistable (or multistable) switching of the resistance of a thin (10–50 nm thick) dielectric films sandwiched between two conductive electrodes when an external voltage is applied between them [2]. The electronic devices whose operation is based on the RS effect are called memristors [3]. The current understanding of the RS mechanism in metal oxides is based on the concept of formation of conductive filaments (CFs), consisting of oxygen vacancies (V$_{0S}$), in the electric field between the electrodes, which shortcut these vacancies (the so-called forming process) [4]. Switching from a low resistance state (LRS) to a high resistance one (HRS) is achieved by the rapture of the CF by a voltage pulse of the appropriate polarity (the so-called RESET process). The CF can be restored by another voltage pulse of the opposite polarity that results in switching from HRS back to LRS (the SET process). The RS mechanism described above is referred to as bipolar RS.
Memristors are considered promising for various applications, e.g. in non-volatile computer memory (the so-called Resistive Random Access Memory, RRAM) [5], in neuromorphic computing [6], etc. However, at present, the widespread use of memristors is limited by insufficient stability of the RS parameters [7]. This is a fundamental property of RS, originating from the stochastic nature of the CF dynamics. Since a limited (countable) number of V_{OS} participates in RS [8], the fluctuations of the RS parameter can significantly exceed their mean values. Traditional approaches to improving RS stability include the selection of appropriate dielectric and electrode materials, engineering the grain boundaries in dielectrics, insertion of electric field concentrators into the dielectric films, etc. [9–11]. Alternative approaches are based on circuit designs, special switching protocols, etc. [12].

In the present study, local RS in ZrO₂(Y) films was investigated by Conductive Atomic Force Microscopy (CAFM) [13] using triangular switching voltage pulses with a superimposed sinusoidal high-frequency (HF) signal. Earlier, the superposition of the HF signal was found to improve the performance and stability of local RS in ZrO₂(Y) films [14, 15]. The effect was attributed to the resonant activation of the O²⁻ ion migration (drift/diffusion) via V_{OS} in an HF alternating electric field. The goal of the present study was to investigate the effect of the superimposed sinusoidal voltage of local RS in ZrO₂(Y) films. In particular, the dependencies of the RS parameters on the HF signal frequency have been investigated. The experimental results were compared with the results of simulation based on the Chua model of an ideal memristor [16].

2. Model

In the present work, we used the model of a current-controlled ideal Chua memristor introduced by Strukov et al. [3]. The parameters of this model are related to the topology and electrical characteristics of the memristor, which are either determined by the fabrication technology or can be measured experimentally. In this approach, the memristor dynamics is described by the following system of equations:

\[ U(t) = [R_{ON}I(t) + R_{OFF}[1 - I(t)]]I(t) \]

\[ \frac{dI}{dt} = \frac{\mu}{L^2} R_{ON} I(t). \]  

(1)

Here \( l(t) \) is the thickness of the highly conductive layer of the dielectric film (with higher V_{OS} concentration) normalized to the total thickness \( L \) of the dielectric, \( R_{ON} \) and \( R_{OFF} \) are the resistances of the memristor in LRS and in the HRS, respectively and \( \mu \) is the mobility of the V_{OS}. Eliminating the current from system (1) and integrating the result over time within the range from 0 to \( t \), we obtain a quadratic equation for \( I \):

\[ I^2 - 2R_{OFF}I + \frac{2\mu R_{ON}}{L^2} w(t) = 0, \]

(2)

where \( w(t) = \int_0^t U(l)dl \), \( \Delta R = R_{OFF} - R_{ON} (R_{ON} < R_{OFF}) \). We need to take only one of the roots of equation (2), which falls into the interval (0, 1). Its analytical expression is

\[ I(t) = \frac{R_{OFF}}{\Delta R} \left[ 1 - \left( 1 - \frac{2\mu R_{ON} \Delta R}{L^2 R_{OFF}^2} w(t) \right)^{1/2} \right], \]

(3)

In this case, the following restriction on the maximum value of the function \( w(t) \) holds:

\[ w_{max} < \left( 1 - \frac{\Delta R}{2R_{OFF}} \right) \frac{L^2 R_{OFF}^2}{\mu R_{ON}}. \]

(4)

Substituting relation (3) into the second equation of system (3) and performing differentiation, we obtain the final expression for the current flowing through the memristor:
\[ I(t) = \frac{R_{\text{OFF}} U(t)}{(\Delta R)^2} \left[ 1 - \frac{2\mu_r R_{\text{ON}} \Delta R}{L^2 R_{\text{OFF}}^2} w(t) \right]^{1/2}. \]  

Relation (5) is general and does not depend on the shape of the voltage applied to the memristor \( U(t) \). In the present work, \( U(t) \) was assumed to be a sum of a low-frequency (LF) sinusoidal driving signal with an amplitude \( A_0 \) and a frequency \( F \), which drives RS and an HF sinusoidal signal with an amplitude \( A << A_0 \) and a frequency \( f >> F \), which activates the \( V_O \) migration:

\[ U(t) = A_0 \sin 2\pi Ft + A \sin 2\pi ft. \]  

Consequently,

\[ w(t) = \frac{A_0}{2\pi F} (1 - \cos 2\pi Ft) + \frac{A}{2\pi f} (1 - \cos 2\pi ft). \]

To account for the effect of resonant activation of the \( V_O \) migration by the HF signal, we introduced a dependence of \( \mu_r \) on \( f \) into the model. To obtain this dependence, we employed the well-known model of motion of a Brownian particle in a two-well potential [17] to describe thermally-activated jumps of \( O^{2-} \) ions onto the adjacent \( V_{OS} \) as an elementary act of the \( V_O \) diffusion process. When the height of the barrier between the wells oscillates with a frequency \( f \) and an amplitude \( \alpha \), the dependence of the mean first passage time \( T_1 \) on \( f \) can be expressed by the approximate formula [18]:

\[ T_1(\lambda) \approx \frac{a^2 (a^2 - 2\lambda)}{2a (a^2 + 2\lambda)} + \frac{2a^2}{(a^2 + 2\lambda)^{1/2}} + \frac{\lambda}{a^2 + 2\lambda}, \]  

where \( a = \alpha/D, \lambda = L^2 f/2D, \) is the spacing between the well minima, \( D \) is the diffusion coefficient in the absence of the oscillating potential, and \( T_1 \) is expressed in units of \( L^2/D \). This approximation is valid when \( \lambda >> a^2 e^{-\alpha} \). The function \( T_1(\lambda) \) (8) has a minimum at

\[ \lambda_0 \approx \frac{a}{\sqrt{2} f} + \frac{1}{2a} \left( \frac{3 + 7}{\sqrt{2}} \right) + \frac{3}{\sqrt{2}} + 1. \]

Accordingly, the mean transition frequency of the particle between the wells \( f_0(\lambda) = [2T_1(\lambda)]^{-1} \) has a maximum at \( \lambda = \lambda_0 \). At \( \lambda \to 0, f_0(\lambda) \) tends to standard the Kramers frequency \( f_k \). Since the process of the \( V_O \) diffusion can be treated as a sequence of elementary jumps of an \( O^{2-} \) ion onto the nearest \( V_{OS} \), one could expect the \( V_O \) diffusion coefficient \( D_0 \) to obey the same dependence on \( f \). In turn, \( \mu_r \) is related to \( D_0 \) by the Einstein’s relation, and its dependence on \( f \) can be expressed as

\[ \mu_r(f) = \mu_{r0}[f(f)/f_k], \]

where \( \mu_{r0} \) is the \( V_O \) mobility in a stationary electric field (figure 1).

![Figure 1](image-url). Calculated dependence of \( \mu_r \) on \( \lambda \) for 3 different values of \( a \).

3. Experiment

A ZrO$_2$(Y) film (≈12% mol. Y$_2$O$_3$) with a thickness \( L \approx 5 \) nm was deposited by HF magnetron sputtering at a substrate temperature of ≈300 °C using a Torr International® 2G1-1G2-EB4-TH1 setup.
We used a Si(001) substrate with a pre-deposited SiO₂ film (≈500 nm thick), a adhesion Ti layer, and a conductive TiN layer (each 25 nm thick). RS in a ZrO₂(Y) film was investigated in ultra high vacuum (UHV) at 300 K using an Omicron® UHV AFM/STM LF1 in the contact mode. The base residual gas pressure inside the AFM/STM chamber was ~10⁻¹⁰ Torr. We used AFM probes coated with a NT-MDT® NSG-11 DCPT™ diamond-like film. The measurement technique was described in [15]. First, the AFM probe was brought into the contact with the ZrO₂(Y) film and adaptive forming was performed by applying a constant voltage \( V_g = 5–6 \) V between the CAFM probe and the TiN sublayer. A digital-to-analog converter (DAC) of an NT-MDT® Solver Pro™ AFM controller was used as an external computer-controlled programmable source of \( V_g \). Once the current through the CAFM probe \( I_i \) reached a preset value of 10–15 nA, \( V_g \) was set to 0 after a 5-10 s pause. Then, the RS performance was tested by acquiring several cyclic current-voltage (\( I-V \)) curves \( I(V_g) \). The ramp voltage \( V_g \) was swept from \( V_{min} = -(4–5) \) V < \( V_{RESET} \) up to \( V_{max} = (5–6) \) V > \( V_{SET} \) and back down to \( V_{min} \). Here \( V_{SET} \) and \( V_{RESET} \) are the switching voltages from HRS to LRS and from LRS to HRS, respectively. The values of \( V_{min} \) and \( V_{max} \) were adjusted to achieve stable RS.

The values of \( I_i \) in LRS and HRS (\( I_{ON} \) and \( I_{OFF} \), respectively) were measured during multiple cyclic write/erase operations using the switching/measurement protocol described in [15]. After applying the triangular switching pulses with amplitudes \( V_{max} \) and \( V_{min} \) and durations \( T_{SET}, T_{RESET} = 1–5 \) s, the values of \( I_{ON} \) and \( I_{OFF} \), respectively were measured at \( V_g = V_{READ} = 3 \) V and \( N_{READ} = 10–20 \) times, and then averaged. The HF sinusoidal signal (\( A = 0.1–2 \) \( \text{V}_f = 0.1 – 25 \) kHz) was superimposed onto the tops of the triangular switching pulses. A built in analog oscillator of NT-MDT® Solver Pro™ AFM controller was used as an HF signal source.

4. Results and discussion
Figure 2 shows the \( I-V \) curve of the CAFM probe contact to the ZrO₂(Y) film (a virtual memristor) measured without an HF signal. A pronounced hysteresis typical for bipolar RS was observed.

Figure 3 presents the model \( I-V \) curves of a virtual memristor calculated according to the model presented in Section 2 for three values of \( \lambda \). The values of \( R_{ON} \) and \( R_{OFF} \) were determined from the experiment. For the averaged values \( I_{ON} \approx 1 \) nA and \( I_{OFF} \approx 0.1 \) nA at \( V_{READ} = 3 \) V (figure 2), we have \( R_{ON} \approx 3 \) GΩ and \( R_{OFF} \approx 30 \) GΩ, respectively. As for \( \mu_{\lambda=0} \), we used the value 4⋅10⁻¹³ \( \text{cm}^2/\text{V}\text{s} \) obtained by measuring the ion migration polarization for the ZrO₂(Y) films (12% mol. \( \text{Y}_2\text{O}_3 \)) deposited in the same conditions [19]. Although the triangular switching pulses were used in the experiment, the simplest LF sinusoidal driving voltage (6) with \( A_{de} = 5 \) V (~ \( V_{SET}, V_{RESET} \)) and \( F = 1 \) Hz was used in the model that allows calculating the functions \( \eta(t) \) (7) easily. Nevertheless, as one can see in figure 3, this simple model reproduces qualitatively the experimental \( I-V \) curve (Figure 2). Moreover, the calculated values of \( I_i \) in figure 3 appeared to be of the same order of magnitude as those measured in the experiment (figure 2).

![Figure 2](image1.png)

**Figure 2.** Cyclic \( I-V \) curve of the CAFM probe contact to the ZrO₂(Y) film.

![Figure 3](image2.png)

**Figure 3.** Model \( I-V \) curves of the virtual memristor for \( \lambda_0(1), 0.5\lambda_0(2) \) and \( 0.1\lambda_0(3) \)
However, there is a significant difference in the shapes of the model curves in figure 3 and the experimental one in figure 2. This difference can be explained as follows. In the CAFM experiment, the tunnel current through a thin insulating layer dominates when $I \rightarrow L$ (when $L - l \leq 1$ nm), which gives a superlinear rise in $I$ as $V_g \rightarrow V_{SET}$ or $V_g \rightarrow V_{RESET}$ in figure 2. The model (3) doesn’t account for this tunnel current, so the model $I-V$ curves in figure 3 have rounded shapes.

As mentioned above, it was previously found that adding an HF sinusoidal signal to the triangular switching pulses improves the local RS performance, in particular, increases the $I_{ON} - I_{OFF}$ difference [14, 15]. The effect was attributed to the resonant activation of the $O^{2-}$ ion migration via $V_{OS}$ under an external alternating electric field. The latter stimulates the jumps of $O^{2-}$ ions onto the adjacent $V_{OS}$ and, thus, promotes the formation and rupture of the CFs under a (quasi)stationary (i.e., slowly varying) external electric field during the SET and RESET processes, respectively.

To verify the above hypothesis, in this work, the dependence of the RS parameters on the HF signal frequency $f$ was measured. Figure 4 shows, the dependence of the $I_{ON} - I_{OFF}$ difference on $f$ for $A = 0.2$ V. A maximum appears at $f_n \approx 5$ kHz. In additional figure 4 shows, the model dependence of $I_{ON} - I_{OFF}$ on $f$, which fits the experimental data ($a$ and $f_n$ were the fitting parameters). One can see a satisfactory agreement of the model curve with the experimental data. Note that the most significant deviation of the model curve from the experiment occurs at lower frequencies (i.e., at small $\lambda$) where the condition $\lambda >> a^2 e^\lambda$ is violated and, hence, the approximate formula (10) is not applicable.

The best fit between the model curve and the experimental data in figure 4 was obtained for $f_n \approx 5.38$ kHz and $a \approx 7$. The latter value gives $\lambda_o \approx 9.83$ according to (11) that, in turns, gives $f_n \approx 1.1$ kHz. This value agrees with the frequency of $O^{2-}$ ion jumps to the nearest neighboring oxygen vacancies in ZrO$_2$(Y) at 300 K (0.4–8 kHz), which was previously estimated in the same virtual memristors by flicker noise spectroscopy [20]. The increase in the hysteresis area of the model $I-V$ curves in figure 3 as $\lambda \rightarrow \lambda_o$ also reflects the resonant behavior of the $I_{ON} - I_{OFF}$ difference with $f$. These results confirm the resonant activation of the $O^{2-}$ ion motion via the $V_{OS}$ to be the origin of the improvement in the RS parameters and the durability in the virtual memristors investigated.

The effect of resonant activation belongs to a wide class of phenomena inherent to stochastic multistable systems (along with stochastic resonance, noise-induced stabilization, etc.) and manifests itself in many fields of physics and chemistry [21].

**Figure 4.** Measured (circles) and model (solid curve) dependencies of the $I_{ON} - I_{OFF}$ difference on $f$ for a virtual memristor formed by the contact of the CAFM probe to the ZrO$_2$(Y) film.

### Conclusion

The results of the present study confirm the resonant activation of the drift/diffusion of $O^{2-}$ ions via oxygen vacancies in an alternating electric field to be the origin of the beneficiary impact of adding a high frequency sinusoidal signal to the triangle switching voltage pulses on the stability of RS at the contact of the CAFM probe to the ZrO$_2$(Y) film on a conductive substrate. These results demonstrate the fundamental properties of the memristor as a stochastic multistable non-linear system.

From a practical point of view, the results of the present study point to the potential of developing innovative switching protocols applicable to next-generation RRAM devices to improve their durability.
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