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Resistive Switching in Individual Ferromagnetic Filaments in $ZrO_2(Y)$/Ni Based Memristive Stacks

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The resistive switching effect in individual ferromagnetic filaments in memristive stacks based on $ZrO_2(Y)$/Ni functional layers was studied experimentally. A conductive probe of an atomic force microscope played a role of a movable top electrode of a virtual memristive stack. The features of bipolar-type resistive switching found were related to the rapture and restoring of the filaments containing Ni atoms in the $ZrO_2(Y)$ dielectric films and are probably caused by different degree of metallization of the filaments. The filaments fromed were manifested in the images obtained by magnetic force microscopy as single-domain ferromagnetic particles.

Keywords: memristor, resistive switching, atomic force microscopy, ferromagnetic filaments.

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Introduction

Random access memory with conductive bridges is actively studied for application as the next generation nonvolatile memory [1–3]. In recent years there is an increase of interest to a possibility of resistive switching (RS) control in memristors by means of magnetic field influence [4,5]. Such possibility provides improved functionality of memristors, allowing to change a current-carrying capability of the conducting filament in dielectric layer of memristor structure (magnetoresistance effect) by means of external magnetic field application [6,7]. Another approach consists in formation of conducting filaments, containing atoms of ferromagnetic material (Co, Ni, Fe), in functional dielectric [8]. This may allow to control the magnetic properties of memristor by means of magnetic or electrical field application to the structure. One of the ways of such approach implementation is creation of at least one of the electrodes of memristive stack from ferromagnetic metal [9]. In this case the formation of ferromagnetic material cations is possible by means of electrochemical reaction of anodic oxidation at the interface of ferromagnetic electrode and dielectric layer and the following formation of filaments of ferromagnetic metal in electrical field between memristive stack electrodes [10].

At the same time, one of the problems in nonvolatile memory memristor devices development is the scaling problem [11]: RS patterns, established during studies of model memristors with electrode sizes, under which the large number of filaments can be formed, are found to be different from RS patterns for memristors with nano-sized electrodes, under which only one filament can be formed.

This study presents the results of experimental studies of mechanisms of individual conducting ferromagnetic filaments forming from ferromagnetic metal atoms and RS specifics of individual conducting filaments of memristive stacks based on $ZrO_2(Y)$/Ni functional layers. Atomic force microscope (AFM) conducting probe is used as the top pressing electrode of memristive stack. Such device (virtual constituent memristor) is a good model system for RS studying [12], since the lateral size of AFM probe contact to dielectric is < 10 nm, that is comparable with filaments sizes in various memristor devices.

1. Experimental procedure

Films of $ZrO_2(Y)$ ($\sim 12\%$ mol. Y_2O_3) with thickness of ~ 10 nm were formed using the method of high frequency magnetron deposition on standard substrates of $TiN(25\,nm)/Ti(25\,nm)/SiO_2(500\,nm)/Si(001)$ with predeposited Ni layer on them with thickness of ~ 10 nm, as well as without Ni layer (samples-satellites). Formation of conducting filaments in memristive stacks, RS studying in them, as well as studying their micromagnetic properties were performed using AFM NT-MDT Solver Pro. Formation of ferromagnetic filaments was performed using AFM probe of HA HR DCP type with electrically conducting diamond like coating by means of sawtooth electric voltage pulses sending between AFM probe and Ni $V_g(t)$ layer with amplitude of ~ 8 V and duration of 6 s (Fig. 1). At the same time the current strength, flowing through AFM probe, $ZrO_2(Y)$ film and Ni (I_t) layer, was controlled. RS effect studying was performed by measuring and analysis

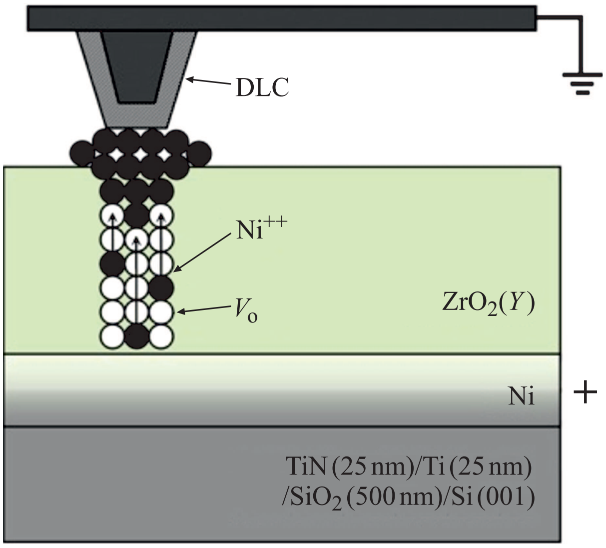

Figure 1. Scheme of ferromagnetic filaments formation and study of RS effect in ZrO_2(Y)/Ni films.

of cyclical VAC of AFM probe contact to ZrO_2(Y)/Ni films. Studying of magnetic fields of formed filaments was performed using magnetic force microscopy (MFM) method using NT-MDT HA_FM_CoFe probes.

2. Results and discussion

Formation of conducting filaments, containing Ni atoms, was performed using AFM probe. For that purpose the probe contacted with a surface of ZrO_2(Y)/Ni film in AFM contact mode and cyclical volt-ampere characteristics (VAC) were measured. Usually the first 5–20 cyclical VAC demonstrated asymmetric hysteresis loops of bipolar type (Fig. 2, *a*, closed curve *1*), conditioned by formation/rupture of conducting filaments, mainly consisting of oxygen vacancies in ZrO_2(Y), electronic conduction on which is performed as per hopping mechanism [13]. Then the conduction nature significantly changed: electrical conductivity of virtual memristive stack in low resistance state (LRS) sharply increased (Fig. 2, *a*, closed curve *2*). At the same time hysteresis loop width increased.

VAC type, presented in Fig. 2, *a* (closed curve *2*), is typical for „conducting bridge“ memristor type [7]. Resistive switching of similar devices is based on rupture and restoring of conducting filaments, consisting of metal atoms, in dielectric film as a result of reduction-oxidation reactions (mainly metal/dielectric interface areas) under electrical field activity [10]. Qualitatively, the mechanism of formation of metallized filament, containing Ni atoms, can be described the following way: at application of positive potential to the bottom active Ni electrode in relation to the top electrode (AFM probe) the ions of Ni^{2+} at the interface of metal layer and oxide, where they are formed due to electrochemical oxidation reaction, are transferred to the oxide by means of electrodiffusion, where, while moving to the direction of AFM probe, they are restored on it, forming the conducting metallized filament, closing the bottom electrode and AFM probe („SET“ process). At the same time the filaments, formed in the beginning of measurements from oxygen vacancies, can facilitate to metal ions drift in the oxide, thus helping to form the metal filaments. We conclude that lateral sizes of formed filaments correspond to the sizes of the area of AFM probe tip contact to the sample surface in terms of value (lateral size is < 10 nm [13]). Only non-linear cyclical VAC (Fig. 2, *b*), contributing to formation and rupture of filaments from oxygen vacancies in oxygen layer (so called reduction-oxidation or RedOx processes), were observed on samples-satellites (without Ni layer) [14].

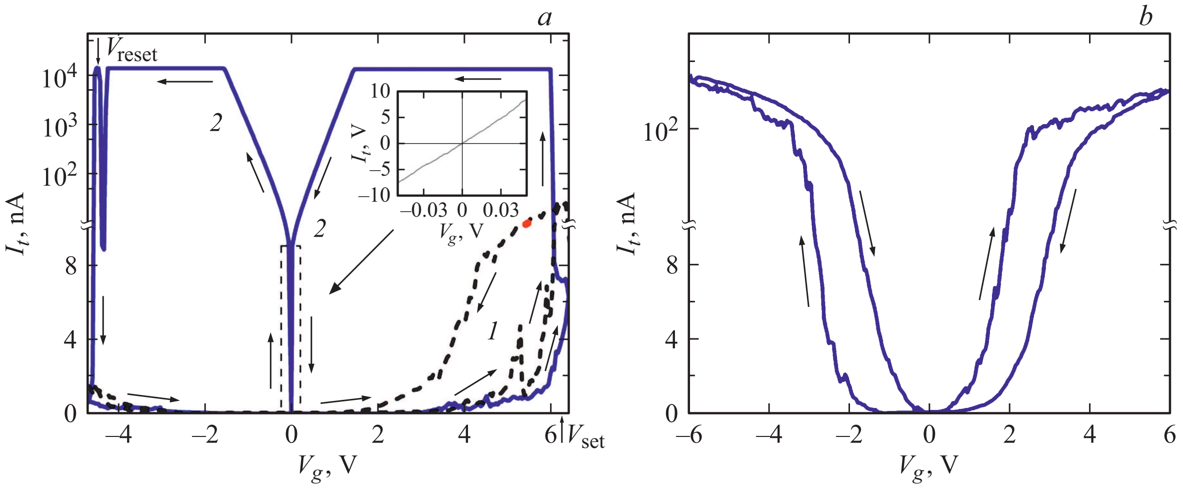

Figure 2. VAC of AFM probe contact to ZrO_2(Y)/Ni film (*a*) and ZrO_2(Y) film without layer of Ni (*b*). Current restriction above level of $1 \cdot 10^4$ nA (*a*) is related to AFM amplifier saturation current. Insert in figure *a* — section of volt-ampere dependence of memristive stack in LRS (closed curve *2*) near 0 in linear scale.

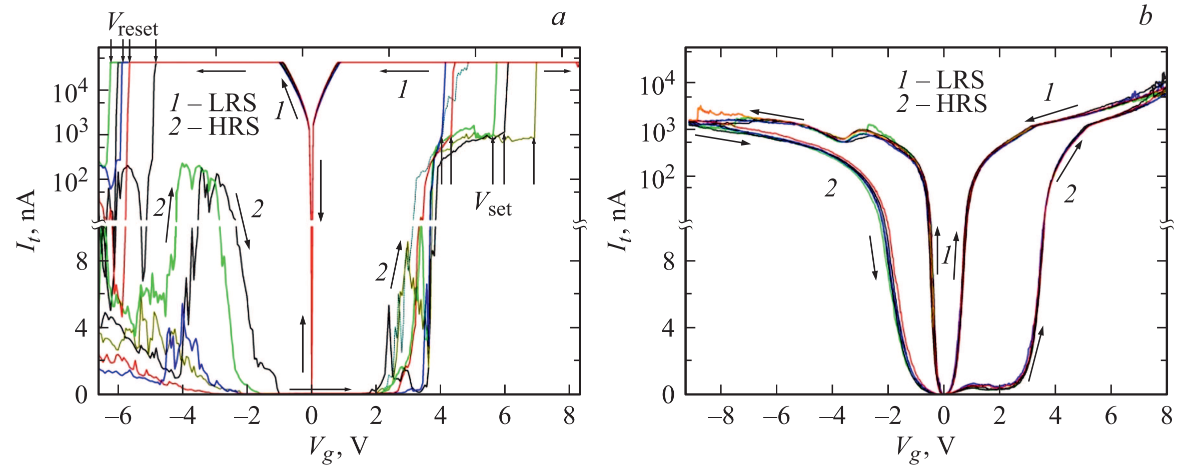

Figure 3. Two types of cyclical VAC (per 5 cycles presented) of AFM probe contact to ZrO_2(Y)/Ni film: *a* — in a mode of metallized filaments formation/rupture; *b* — filament metallization was not complete. Current restriction above level of $1 \cdot 10^4$ nA (*a*) is related to AFM amplifier saturation current. LRS — low resistance state, HRS — high resistance state.

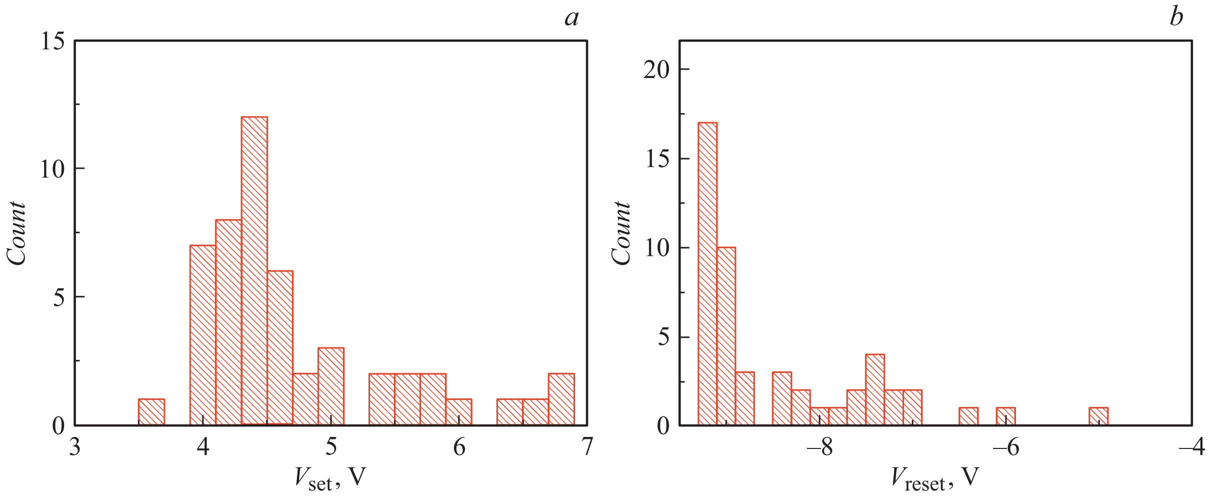

Figure 4. Bar charts of distribution of V_{set} (*a*) and V_{reset} (*b*) of virtual memristive stack based on ZrO_2(Y)/Ni film in a mode of metallized filaments formation.

Cyclical VAC of AFM probe contact to ZrO_2(Y)/Ni layers surface after Ni filament formation (molding procedure) demonstrated stable resistive switching of bipolar type with hysteresis loop of two types (Fig. 3). At the same time both VAC types can be observed on a single virtual memristor device and defined by selection of sweep as per voltage applied between AFM probe and a sample. Cyclical VAC, presented in Fig. 3, *a*, are related, in our opinion, to formation/rupture of metallized filaments, closing the Ni layer to AFM probe. Ratio of currents, flowing through the stack in LRS and in high resistance state (HRS), is $(I_{\text{LRS}}/I_{\text{HRS}}) > 5000$ at $V_g = 0.5$ V. The main RS parameters spread, observed at cyclical VAC, presented in Fig. 3, *a*, is caused by the fact that, due to stochastic nature of filament structure formation, its previous current-carrying capability is not reproduced. Non-complete filament „metallization“ can also be implemented. In this case the conductivity is conditioned by mixed or activation nature of conductivity depending on thickness of dielectric layer between filament and AFM probe (Fig. 3, *b*). The average current ratio in this case is $\langle I_{\text{LRS}}/I_{\text{HRS}}\rangle \sim 10$ at $V_g = 0.5$ V. Bar charts of distribution of the main RS parameters (V_{set}, V_{reset}), built based on analysis of 50 cyclical VAC in metallized filament formation/rupture mode, are presented in Fig. 4.

It is established that V_{set} value for such memristive stacks changes in a range from 3.5 to 7 V (Fig. 4, *a*). At the same time the bar chart of distribution of Vreset (Fig. 4, *b*) demonstrates that electric switching voltage in negative area changes in a range from −9.2 to −5 V and has two peaks at $V_g = -9.2$ and $= -7.5$ V.

Fig. 5 shows the dynamics of values changes of I_{LRS} and I_{HRS} during 100 switching cycles in the mode of metallized filaments formation/rupture (Fig. 5, *a*) and in case when filament metallization was not complete (Fig. 5, *b*).

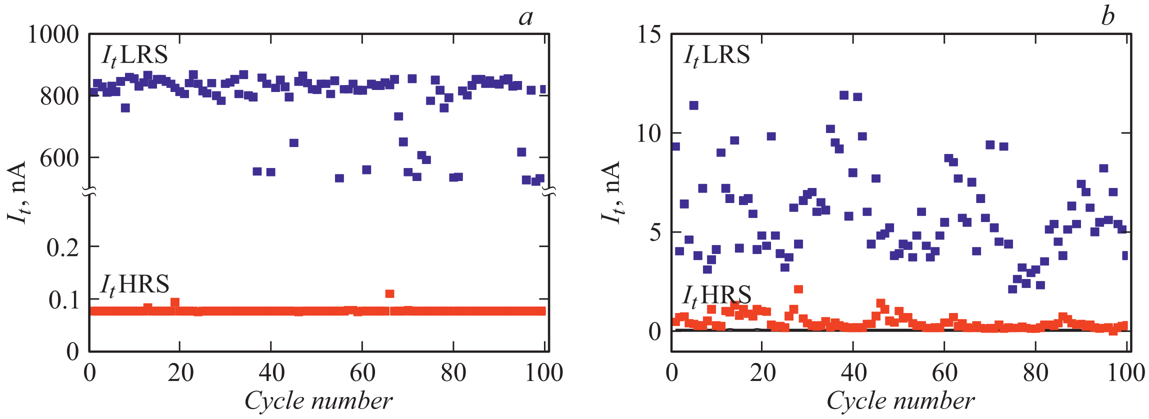

Figure 5. Dynamics of values changes of I_{LRS} and I_{HRS} during 100 switching cycles in the mode of metallized filaments formation/rupture (*a*) at $V_g = 0.5\,\text{V}$ in case when filament metallization was not complete (*b*).

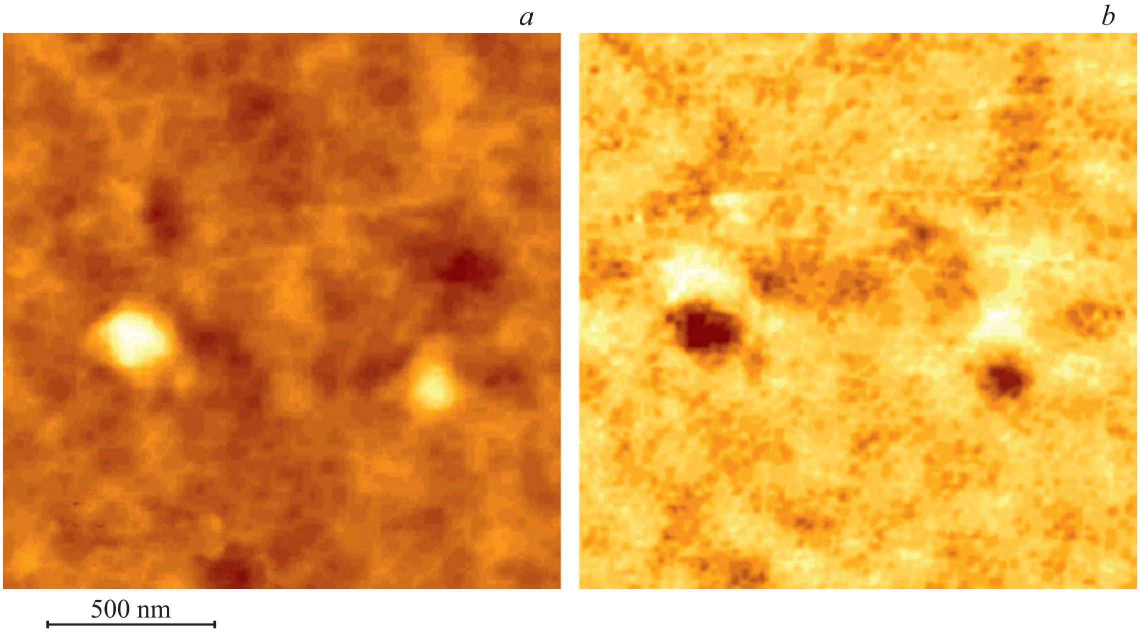

Figure 6. Morphology (*a*) and MFM contrast (*b*) of ZrO_2(Y)/Ni film surface after formation of two conducting filaments.

Based of presented results it can be concluded that in the observed device with metal conducting filament the implementation of two conducting states is possible. RS in such device is conditioned by two different conduction mechanisms (metal, activation).

Study of magnetic properties of the formed filaments was performed using MFM method. Morphology of ZrO_2(Y)/Ni film surface (Fig. 6, *a*) in places of metallized filaments formation demonstrates formation of flat islands with height of 1–1.5 nm and lateral size of 100–150 nm, which are revealed on MFM image (Fig. 6, *b*) as single-domain ferromagnetic particles [15].

This may be related to accumulation of Ni atoms in near-surface layer of ZrO_2(Y) film near conducting filament during its formation. There were no magnetic contrast from formed filaments on MFM images of samples-satellites after conducting filaments formation (in LRS).

Conclusion

Thus, the study experimentally demonstrated a possibility of virtual memristor creation based on stabilized zirconium dioxide ZrO_2(Y) with sublayer of Ni with conducting filaments of atoms of Ni-„conducting bridge“ using AFM probe. Possibility of such device operation in two modes ($I_{\text{LRS}}/I_{\text{HRS}} \sim 10$ and $I_{\text{LRS}}/I_{\text{HRS}} > 5000$ at $V_g = 0.5\,\text{V}$), presumably related to different degree of filament metallization during RS process, is demonstrated. Formed conducting filaments, containing Ni atoms in ZrO_2(Y)/Ni functional layer, exhibit ferromagnetic properties and revealed on MFM images as single-domain particles.

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Conflict of interest

The authors declare that they have no conflict of interest.

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