Threshold and Memory Switching in Oxides of Molybdenum, Niobium, Tungsten, and Titanium

V. P. Malinenko, A. L. Pergament, O. V. Spirin, V. I. Nikulshin

Abstract **— In this paper we report on the study of electrical switching in thin film MOM structures on the basis of transition metal oxides under AC conditions. The materials studied are Nb_2O_5, TiO_2, and WO_3, obtained by electrochemical oxidation of the metal, as well as MoO_3, obtained by thermal deposition in vacuum. Transformations of dynamic switching characteristics with changes in temperature and frequency are investigated. The possibility of appearance of both monostable switching and memory switching in the same material is shown. It is also shown that doping of film structures of anodic titanium oxide with aluminum ions leads to a significant stabilization of dynamic current-voltage characteristics and long-term reproducible operation of the switching structures metal/TiO_x:Al /metal.**

Index Terms **— threshold switching, resistive memory, transition metal oxides, electrical properties, *I-V* characteristics.**

I. Introduction

It is known that many transition metal oxides (TMOs) exhibit threshold – i.e. monostable, without any memory effects – switching [1]. Generally, electrical switching of a kind can be observed in a great variety of materials in many different forms and structures [2]. Current-voltage characteristics of such systems are usually classified into two categories: those with S-type and with N-type negative differential resistance (NDR) – see Fig. 1. N-type switching is also often referred to as “VCNR” (voltage-controlled negative resistance), and S-type – as “CCNR”, i.e. current-controlled negative resistance. As a rule, these phenomena are observed in amorphous insulators and semiconductors, TMOs included.

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Electronic switching in amorphous thin films can be divided into two general types: (a) monostable threshold switching, in which continuous electrical power is required to maintain the highly conducting ON state; and (b) bistable memory switching, in which both ON and OFF states can be maintained without electrical power (just this kind of switching is described in the beginning of this section). In other words, for threshold switching, the OFF-to-ON transition is absolutely reversible and repetitive, whereas for memory switching, a large voltage pulse is usually applied in the erase operation cycle to switch a device from the ON back to OFF state [2].

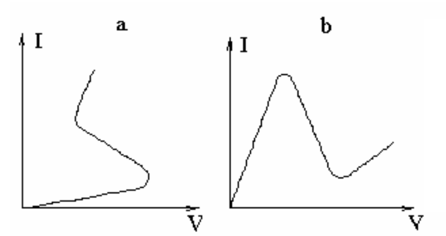
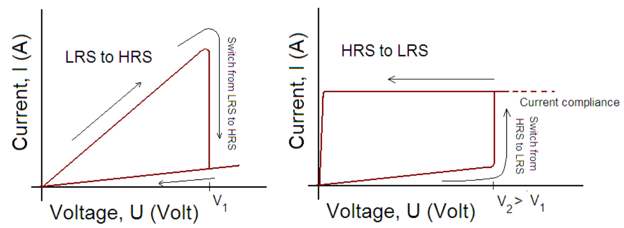


Fig. 1. *I-V* curves with (a) S-type and (b) N-type NDR [2].

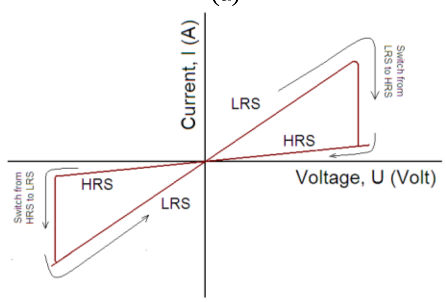
The effect of resistive memory switching is a sharp and reversible transition of materials between two states with a different resistance. Switching is observed in a large class of compounds: complex perovskite oxides, organic compounds, binary metal oxides, mostly, transition metal oxides such as NiO, CuO, ZnO, TiO_2, Nb_2O_5, Ta_2O_5, ZrO_2, HfO_x etc. [3].

Resistive Random Access memory (ReRAM) is an electronic memory which is based on resistive switching effect. The ReRAM memory cell has a capacitor-like structure (metal/insulator/metal) in which an oxide layer is located between two metal electrodes. Under the voltage pulses ReRAM cells switch between high resistance state (HRS) and low resistance state (LRS). HRS and LRS represent logical “1” and “0”; they are nonvolatile, stable in time, states.

In appearance of current–voltage characteristics switching behavior (ReRAM operations) can be divided into two broad classes: unipolar and bipolar (Fig. 2). Switching is called unipolar (or symmetric) when the switching procedure does not depend on the polarity of the voltage and current signal, it depends only on amplitude. Bipolar switching requires an alternating polarity of the applied signal. This type of switching is described in numerous papers (see [3] and references therein). The same material can show both bipolar and unipolar switching. Type of switching depends on materials of electrodes, properties of oxide layer, interface between oxide and electrode, and conditions of electrical forming (EF) process.



(a)



(b)

Fig. 2. (a) Typical *I-V* characteristics of the unipolar resistive switching effect. (b) A typical *I-V* characteristic of the bipolar resistive switching effect [3].

In this work we have investigated electrical switching in oxides of Mo, Nb, W, and Ti. The aim of the present study is to establish the basic regularities of the switching effect in thin-film structures based on the above-listed TMOs and to determine dependences of the switching parameters on temperature and frequency.

II. Experimental Methods

Oxide films were prepared by anodic oxidation [4]. For niobium, oxidation was carried out in electrolytes based on 10 % and 0.1 % solutions of orthophosphoric acid (H_3PO_4) at a current density of 15 mA/cm^2, and an anodic voltage was V_a = 20 V. Tungsten and titanium were anodized as described elsewhere [1], [2], and molybdenum oxide was obtained by vacuum evaporation [5] onto glass/SnO_2 substrates.

Anodic oxide films (AOF) on Ti were also obtained in 5% water solution of citric acid ($C_6H_8O_7$), in volt-static regime at V_a of 20 and 40 V. Some samples anodized at 40 V were doped with aluminum by means of adding soluble Al-containing substances to the electrolyte. For the insertion of Al^{3+} ions into the AOF, the process of doping was carried out at cathodic polarization.

Current-voltage characteristics of the samples were measured in sandwich geometry structures with the spring-loaded top electrode (Au wire 0.5 mm in diameter), and the bottom electrode was either corresponding metal substrate (Nb, W or Ti) in the case of an anodic oxide, or transparent conductive coating, tin dioxide, – in case of Mo oxide. Samples were subjected to preliminary electroforming at an AC voltage, close to the breakdown voltage, for a certain time. The EF process and *I-V* curves after forming were investigated by the oscillographic method [1], [2], [5] (Fig. 3) in the AC dynamic mode using a digital oscilloscope OWON PDS 5022S with filing the data to a PC via a USB-cable.

Temperature measurements were performed as follows. A heating element was added to the sample studied, connected to a source of direct current ("8" in Fig. 3) to change the temperature. The temperature was monitored by a thermocouple attached to a voltmeter ("11" in Fig. 3).

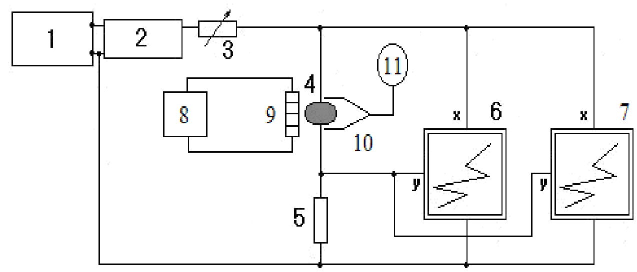
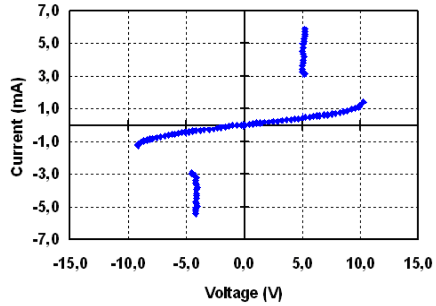


Fig. 3. Installation diagram for the study of the *I-V* curves and their temperature dependences: 1 – low-frequency signal generator (G3-112/1); 2 – amplifier of G3-112/1; 3 – variable load resistor (R_L); 4 – sample (with resistance R_o); 5 - current measuring resistor (50 Ω); 6 – analog oscilloscope C1 - 220; 7 – digital oscilloscope OWON PDS 5022S; 8 – DC power source B5-76/1; 9 – resistive heater; 10 – Cu-constantan thermocouple; 11 – voltmeter B7-40/4.

III. Results and Discussion

The voltage-current characteristic for the electroformed niobium-AOF-metal structure is shown in Fig. 4. The parameters of the structures (threshold voltage V_{th} and current I_{th}, resistances of OFF and ON states) may vary by up to an order of magnitude from point to point for the same specimen. Such a wide range of variation of the V_{th} and R_{off} values, as well as the absence of a correlation between these switching parameters and the parameters of the sandwich structures (the electrode material and area, the film thickness), leads to the conclusion that resistance and threshold parameters are mainly determined by the forming process [2]. Conditions of the EF process cannot be unified in principle, because the first stage of forming is linked to breakdown, which is statistical in nature. As a result, the diameter and phase composition of the channel (and, consequently, its effective specific conductivity) vary with position in the sample. This accounts for the scatter in the parameters and for the seeming absence of their thickness dependence. However, usually the threshold voltage value lies in the range ~10–15 Volts (Fig. 4, a). Similar behavior has been observed for other materials – see Figures 4, b and c.

The temperature dependence of the threshold voltage for one of the samples (Ti oxide) is presented in Fig. 5. As one can see, it is quite usual for switches based on TMOs [1] and corresponds to the “critical temperature” model [5]. It should be noted however that, e.g., for the Nb oxide-based samples, V_{th} has been found to be almost independent of temperature in the range from RT up to 380 K.



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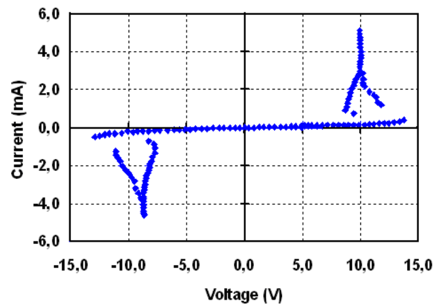

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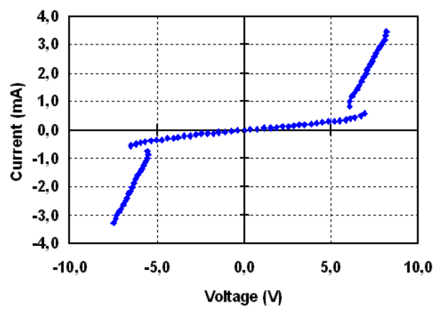


(c)

Fig. 4. (a) *I-V* curves for (a) Nb oxide, (b) Mo oxide on SnO_2, and (c) W oxide film MOM structures at RT and f = 100 Hz.

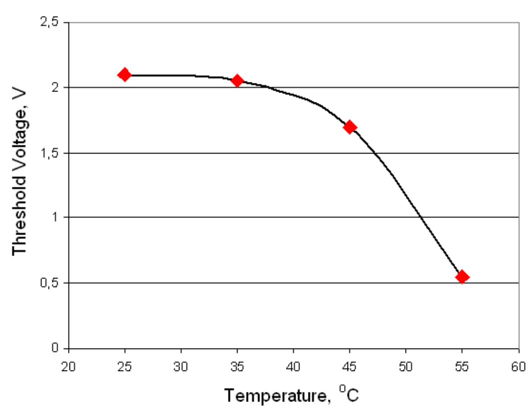
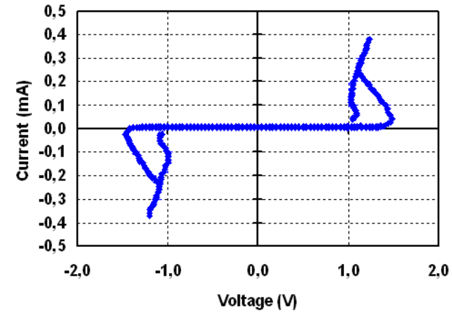


Fig. 5. The value of V_{th} as a function of temperature for the Ti–TiO_x–Au switching structure at f = 250 Hz. AOF on Ti is obtained in voltstaic regime in 0.5 % aqueous solution of $C_6H_8O_7$ at V_a = 20 V.

Next we have studied the dependences of the switching parameters of the TiO_x-based samples on the input AC voltage



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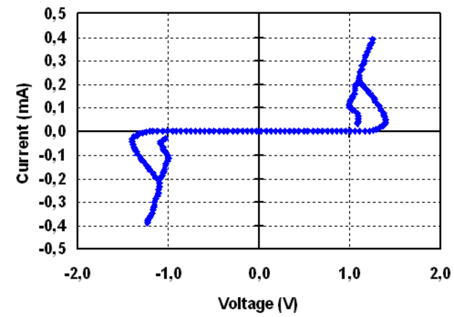

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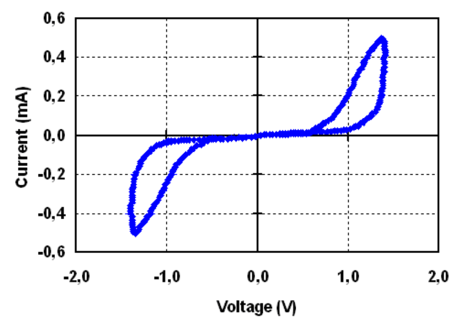


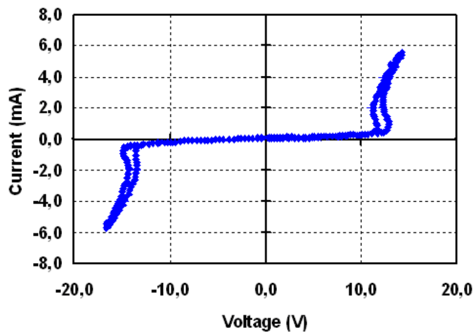
(c)

Fig. 6. Switching of a sample on the basis of TiO_2 film at different frequencies: (a) 100 Hz, (b) 10 kHz, and (c) 1 MHz.

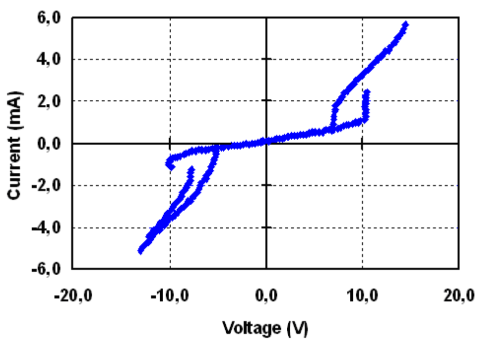
frequency (monitored by means of a generator G3-112/1, "1" in Fig. 3) with the use of a digital oscilloscope which allows for the data memorization. These *I-V* characteristics are presented in Fig. 6.

It can be seen from the figure that at frequencies higher than 10 kHz, monostable threshold switching transforms into the bistable memory switching effect. This resistive switching is of a unipolar type (see Fig. 2 (a), right panel).

For the samples doped with Al, we encountered the effect of stabilization of the switching characteristics. The point is that usually the *I-V* curves might spontaneously slightly change their parameters with time during operation and, moreover, after several thousands switching cycles, the S-shaped *I-V* curve could completely degrade and switching no longer occurs. The above-described behavior is typical of pure non-doped samples, while for the structures based on AOF TiO_2:Al the behavior is radically different. For these samples, threshold voltage is also in the range 10 to 15 V (Fig. 7), but current-voltage characteristics demonstrate stability and long-term reproducible operation (up to 10^{10} cycles without a noticeable change in the threshold parameters). It can be assumed that the stabilization of the switching parameters is caused by a change in the energy-band structure of titanium oxide as a result of doping.



(a)



(b)

Fig. 7. *I-V* curves of Al-doped TiO_x; (a) and (b) – two different samples.

It is known that the switching effect in thin film MOM structures on the basis of TMOs is associated with metal-insulator transition [1], [2], [5]. In this case, the switching mechanism might be described in terms of the “critical temperature” model. Due to the effect of Joule heating, when the voltage reaches a critical value $V = V_{th}$, the switching channel is heated up to $T = T_t$ (where T_t is the temperature of the phase transition) and the structure undergoes a transition from the insulating OFF state to the metallic ON state. The channel is formed under the electrode during electroforming due to crystallization and partial reduction of the initial oxide. In the case of electroforming of the structures based on Nb and Ti oxides, the most energetically favorable (in terms of a minimum Gibbs free energy in the corresponding reactions of the highest oxide reduction) is the formation of the channels consisting of Ti_2O_3 and NbO_2, respectively [1]. The value of T_t in niobium dioxide is rather high, 1070 K [1], therefore we do not observe any temperature dependence of V_{th} in a limited temperature range in the vicinity of RT. On the other hand, for Ti_2O_3, the transition into metallic state commences at $T \sim 400$ K [6]. However, in Fig. 5 we see that V_{th} tends to zero at $T \sim 330$ K. Such a lowering of T_t might be due to the fact that the metal-insulator transition occurs at switching in a high electric field (~10^6 V/cm) [7].

Next we discuss the effect of stabilization of the switching parameters by means of doping and the observed appearance of both monostable switching and memory switching in the same material, namely in titanium oxide. The former effect is known in the literature; particularly, similar phenomenon has been described in [8]. In this work the memory effect has been observed in Er stabilized β-MnO_2 metal-oxide-semiconductor structure. The electric properties and mechanism of charge tunneling and trapping have been studied by combining frequency-dependent capacitance-voltage curves, variable sweep range capacitance-voltage curves, and current-voltage curves. The charge traps are identified to be deep donors in β-MnO_2. The deep donor level is close to the valance band, which results in the asymmetric enlargement in variable sweep range capacitance-voltage curves. These experiments show that erbium-doped β-MnO_2 is a good candidate charge storage material in nonvolatile memory devices [8]. As to the coexistence of threshold and memory switching in the same material [2] (as well as the coexistence of unipolar and bipolar resistive switching in, e.g., NiO thin films [9]), these phenomena are also well known and described in the literature. However, unlike in most cases where the type of switching depends on electrode materials or electroforming conditions, in our case it depends on frequency (Fig. 7).

IV. Conclusion

In summary, electrical switching in thin film MOM structures on the basis of transition metal (Nb, Ti, W, and Mo) oxides under AC conditions are studied. Changes in switching characteristics depending upon temperature and frequency are particularly investigated. It is shown that the threshold switching effect is associated with the metal-insulator transition, and the temperature dependence of the threshold voltage for titanium oxide corresponds to the “critical temperature” model. At frequencies higher than 10 kHz (and up to 1 MHz), the threshold switching effect transforms into bipolar resistive memory switching. For the samples doped with Al, the effect of stabilization of the switching characteristics is found. It is assumed that the stabilization of the switching parameters is caused by a change in the energy-band structure of titanium oxide as a result of doping.

References

[1] F. A. Chudnovskii, L. L. Odynets, A. L. Pergament, G. B. Stefanovich, "Electroforming and switching in oxides of transition metals: The role of metal-insulator transition in the switching mechanism", *J. Solid State Chem.*, vol.122, pp. 95-99, 1996.

[2] A. Pergament, G. Stefanovich, A. Velichko, V. Putrolainen, T. Kundozerova, and T. Stefanovich. "Novel Hypostasis of Old Materials in Oxide Electronics: Metal Oxides for Resistive Random Access Memory Applications" In: *Research in Novel Materials* (Editor: Rafiqul Islam), New York: Nova Science Publishers, 2013, pp. 77-104.

[3] T. V. Kundozerova and G. B. Stefanovich. "Unipolar Resistive Switching Effect" In: *Oxide Electronics and Functional Properties of Transition Metal Oxides* (Editor: A. Pepgament), New York: Nova Science Publishers, 2014, pp. 1-30.

[4] L. L. Odynets and V. M. Orlov, *Anodic Oxide Films*, Leningrad: Nauka, 1990 [in Russian].

[5] A. L. Pergament, V. P. Malinenko, L. A. Aleshina, E. L. Kazakova, and N. A. Kuldin, "Electrical Switching in Thin Film Structures Based on

Molybdenum Oxides", *Journal of Experimental Physics*, vol. 2014, Article ID 951297, 6 pages, 2014.

[6] N. F. Mott, "Metal-insulator transition in Ti_2O_3", *Journal de Physique*, vol. 42, no. 2, pp.277-281, 1981.

[7] G. Stefanovich, A. Pergament, and D. Stefanovich, "Electrical switching and Mott transition in VO_2", *Journal of Physics: Condensed Matter*, vol. 12, no. 41, pp. 8837-8845, 2000.

[8] J. Cui, T. Ji, T. Nie, and Z. Jiang, "Charge tunneling and trapping in Er stabilized β-MnO_2 films for memory applications", *Appl. Phys. Lett.* vol. 104, pp. 263508, 2014.

[9] D. Choi and C. S. Kim, "Coexistence of unipolar and bipolar resistive switching in Pt/NiO/Pt", *Appl. Phys. Lett.* vol.104, pp. 193507, 2014.