Electrical switching in metal-oxide-metal structures based on anodic niobium oxide

A L Pergament and P P Boriskov
Institute of Physics and Technology, Petrozavodsk State University, 33 Lenin str., Petrozavodsk, 185910, Russia
E-mail: boriskov@petrsu.ru

Abstract. Nonlinear current-voltage (I-V) characteristics with S-type negative differential resistance, as a characteristic feature of the switching effect, are inherent in a variety of transition metal oxides, niobium oxide included. Although this phenomenon has been known for a long time, recent proposals to use oxide-based switching devices as elements of oscillatory neural networks have resumed the interest in this area. In this work, electrical switching in sandwich structures based on anodic films of niobium oxide is studied. After being electroformed, these structures exhibit S-shaped I-V characteristics. As the temperature increases, the threshold voltage decreases, presumably tending to zero at a critical temperature $T_0$, which correlates with the temperature of metal–insulator phase transition of niobium dioxide. Channels consisting of NbO$_2$ are formed in the initial anodic films during the process of electroforming.

1. Introduction
Niobium forms several oxides, among which the most stable are insulating Nb$_2$O$_5$, metallic NbO, and NbO$_2$ demonstrating metal-insulator transition. Due to their diverse and interesting physical properties, many applications of niobium oxides have been proposed in recent years, including solid electrolytic capacitors, catalysts, electrochromic devices, transparent conductive oxides or memristors [1]. Also, threshold and memory switching in thin-film metal/oxide/metal (MOM) structures based on niobium oxides is of interest for neuromorphic computing applications [2-7]. An oscillatory neural network (ONN) is one of the most promising approaches for development of the next generation computing architectures realizing the brain-inspired massively parallel computing paradigm [8]. In ONNs, an elementary cell comprises an oscillator circuit, and the cells are locally coupled by resistors or capacitors.

Vanadium dioxide is currently considered as one of the key materials for neuromorphic oxide electronics [9]. Two-terminal thin-film MOM devices based on VO$_2$ exhibit S-type switching [7-9], and in an electrical circuit containing such a switching device, relaxation oscillations are observed under certain conditions, namely, when the load line intersects the $I$-$V$ curve at a single point in the negative differential resistance (NDR) region. The switching effect in vanadium dioxide is caused by the metal-insulator transition (MIT) occurring in this material at $T_t = 340$ K [9].

VO$_2$ is beneficial as a model object for simulating neural networks, while at the same time it is more convenient to use NbO$_2$ for the manufacture of industrial components of neural circuits, since the switches based on it operate in a wider temperature range and satisfy the requirement to work at
temperatures of up to 600 K. Note that NbO\(_2\) has a higher \(T_t\) (~1070K [10]) and lower leakage current due to its large band gap (1.0 eV) as compared to that of VO\(_2\) (0.67 eV) [4].

In this work we report the results on electroforming and switching in MOM structures with thin-film oxides of niobium. The oxide films are obtained by electrochemical anodic oxidation of Nb metal. Our main concern is to investigate the temperature dependence of the threshold voltage, for these data are required in order to understand the switching mechanism and, on the other hand, they are necessary for practical applications of the switching devices.

2. Experimental methods
The sandwich MOM devices under study were fabricated by oxidation of the metal substrates: both polished niobium foils and vacuum-deposited layers. Au electrodes were vacuum-evaporated onto the surfaces of oxide films to complete the MOM structure (figure 1a), and spring-loaded point contacts, made of titanium wires 0.5 mm in diameter, were also used. The oxidation was carried out electrochemically, under anodic polarization in an electrolyte (0.1 N aqueous solution of phosphoric acid). Anodic oxidation permits the synthesis of high quality homogeneous amorphous niobium oxide films, and their phase composition corresponds to Nb\(_2\)O\(_5\) [11]. Anodizing voltage under galvanostatic conditions was 50 V which gave the film thickness of 120 nm.

![Figure 1. (a) The sandwich switching structure (schematic): (1) niobium metal substrate, (2) anodic oxide film, (3) top metal contact, and (4) switching channel (NbO\(_2\), as is discussed below in Section 3). (b) Measurement circuit: (1) ac power supply, (2) MOM structure, (3) oscilloscope; \(R_L\) – load resistor.](image)

The \(I-V\) characteristics of initial structures and those obtained during and after electroforming were investigated using the ac oscillographic method (figure 1b). The temperature dependences of the switching parameters were investigated in the range from 293 to 600 K in air, and the temperature was measured with a copper-constantan thermocouple.

3. Results and discussion
The current-voltage characteristics of the initial structures are nonlinear and slightly asymmetric. The resistance at zero bias, measured with the point contact, is over \(10^8\) \(\Omega\). When the amplitude of the applied voltage reaches the electroforming voltage, a sharp and irreversible increase in conductivity is observed and the \(I-V\) curve becomes S-shaped with the threshold voltage \(V_{th}\) \(\approx\) 10 V (figure 2).
As the temperature increases, $V_{th}$ decreases tending to zero at some finite temperature $T_0$ (figure 3). This is best exhibited by the vanadium oxide structures (the $V_{th}(T)$ curve for vanadium is presented in figure 3 for comparison). The values of $T_0$ vary considerably for different oxides, but they are nearly identical for different structures of the same oxide. For the Nb-Nb$_2$O$_5$-metal structures, it was impossible to measure the $V_{th}(T)$ relationship over the whole temperature range, because heating above 300 °C induced processes related to diffusion and change in the channel phase composition, leading to degradation of the switching structure. Nevertheless, it is evident from the experimental curve 1 of figure 3 that, for the niobium oxide, the value of $T_0$ exceeds 600 K.

During electroforming, current-induced heating of the film under the electrode leads to a diffusion of both metal from the substrate into the film and oxygen from the outer layer to the inner one. Also the transport of metal and oxygen ions due to the applied electric field is possible. Since during electroforming (unlike thermal or electrochemical oxidation) no external oxygen is present, no reaction can take place except the reduction of the highest oxide. The reduction results in growth of the channel, consisting of a lower oxide, through the film from one electrode to another. These lower oxides are VO$_2$ in case of vanadium anodic oxide and NbO$_2$ in case of niobium anodic oxide, which is confirmed by thermodynamic calculations [12].
Thus, the S-shaped current-voltage characteristic is conditioned by the development of an electrothermal instability in the channel. When a voltage is applied, the channel is heated up to $T = T$, (at $V = V_\text{th}$) by the current and the structure undergoes a transition from the high-resistance OFF insulating state to the low-resistance ON metallic state. As the temperature increases, $V_\text{th}$ decreases, tending to zero at $T = T$. For the niobium oxide, the heating up to 600 K leads to a change in the channel phase composition, resulting in degradation of the switching structure, and above this temperature switching no longer occurs.

4. Conclusion
In summary, we have reported the electrical switching effect in MOM structures based on niobium anodic oxide. This switching with an S-shaped current-voltage characteristic is associated with the insulator–metal transition in NbO$_2$ occurring in an electric field. The channels, consisting of niobium dioxide, are formed in initially produced anodic films during preliminary electroforming. Note that in the work [7], the oscillatory circuits have been studied by modeling using experimental I-V characteristics of a NbO$_2$ switch with a stable NDR region and a VO$_2$ switch with an unstable NDR, considering the temperature dependences of the threshold characteristics. These results are relevant for modern neuroelectronics and have practical significance for the introduction of the neurodynamic models in circuit design and brain-machine interface.

Acknowledgement
This research was supported by the Russian Science Foundation (grant no. 16-19-00135).

References
[1] Nico C, Monteiro T and Graça M P F 2016 Niobium oxides and niobates physical properties: Review and prospects Progress in Materials Science 80 1-37
[2] Nandi S K, Li S, Liu X and Elliman R G 2017 Temperature dependent frequency tuning of NbO$_2$ relaxation oscillators Appl. Phys. Lett. 111 202901
[3] Kumar S, Strachan J P and Williams R S 2017 Chaotic dynamics in nanoscale NbO$_2$ Mott memristors for analogue computing Nature 548 318–21
[4] Lee D, Cha E, Park J, Sung C, Moon K, Chekol S A and Hwang H 2018 NbO$_2$-based frequency storable coupled oscillators for associative memory application IEEE Journal of the Electron Devices Society 6 250-3
[5] Li S, Liu X, Nandi S K, Venkatachalam D K and Elliman R G 2017 Coupling dynamics of Nb/NbO$_2$ relaxation oscillators Nanotechnology 28 125201
[6] Gao L, Chen P-Y and Yu S 2017 Exploiting NbO$_2$ metal-insulator-transition device as oscillation neuron for neuro-inspired computing IEEE Electron Devices Technology and Manufacturing (EDTM) Conference 152-3
[7] Boriskov P and Velichko A 2019 Switch Elements with S-shaped Current-Voltage Characteristic in Models of Neural Oscillators Electronics 922, 1-20
[8] Pergament A, Velichko A, Belyaev M and Putrolaynen V 2018 Electrical switching and oscillations in vanadium dioxide Physica B: Physics of Condensed Matter 536 239-48
[9] Pergament A L, Stefanovich G B and Velichko A A 2013 Oxide Electronics and Vanadium Dioxide Perspective: A Review J. Selected Topics in Nanoelectronics and Computing 1 24-43
[10] Gallego J M and Thomas C B 1982 Phase transitions in films of niobium dioxide Solid State Comm. 43 547-9
[11] Dell’Oca C J, Pulfrey D L and Young L 1971 Anodic Oxide Films Physics of Thin Films 6 1-79
[12] Pergament A, Stefanovich G, Malinenko V and Velichko A 2015 Electrical Switching in Thin Film Structures Based on Transition Metal Oxides Advances in Condensed Matter Physics 654840