Multifilamentary character of anticorrelated capacitive and resistive switching in memristive structures based on \((\text{CoFeB})_x(\text{LiNbO}_3)_{100-x}\) nanocomposite

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Abstract
Resistive and capacitive switching in capacitor metal/nanocomposite/metal structures based on \((\text{CoFeB})_x(\text{LiNbO}_3)_{100-x}\) nanocomposite (NC) fabricated by ion-beam sputtering with metal content \(x \approx 8\text{–}20\) at. \% is studied. The peculiarity of the structure synthesis was the use of increased oxygen content \((\approx 2\cdot10^{-5}\) Torr\) at the initial stage of the NC growth. The NC films, along with metal nanogranules of 3–7 nm in size, contained a large number of dispersed Co (Fe) atoms (up to \(\sim 10^{22}\) cm\(^3\)). Measurements were performed both in DC and AC (frequency range 5–13 MHz) regimes. When switching structures from high-resistance \((R_{\text{off}})\) to low-resistance \((R_{\text{on}})\) state, the effect of a strong increase in their capacity was found, which reaches 8 times at \(x \approx 15\) at. \% and the resistance ratio \(R_{\text{off}}/R_{\text{on}} \approx 40\). The effect is explained by the synergetic combination of the multifilamentary character of resistive switching and structural features of the samples associated, in particular, with the formation of high-resistance and strongly polarizable LiNbO\(_3\) layer near the bottom electrode of the structures.
I. INTRODUCTION

Structures of the type of metal/oxide/metal (MOM), demonstrating the effects of reversible resistive switching (RS), are very promising for creating multilevel memories and memristor arrays for emulate synapses in the development of neuromorphic (bio-inspired) computational systems to solve the so-called anthropomorphic problems: image and natural language recognition, decision-making, generalization, prediction, etc. [1–11]. Such systems possess low power consumption and can essentially surpass modern computer systems based on von Neumann architecture by efficiency of information processing (speed and reliability) at performance of the cognitive functions listed above.

Over the last decade, a sufficiently large number of different MOM memristive structures were discovered and studied. They can be divided into several basic types depending on the RS mechanism. First of all, it should be noted that the RS effects in the most studied MOM structures are associated with the processes of electromigration of oxygen vacancies in the oxide layer (TiO$_x$, TaO$_x$, HfO$_x$, etc.), or metal cations such as Cu, Ag into the dielectric (e.g., SiO$_2$) from the active electrode of the MOM structure [1, 7–15]. In these cases, RS of the structure to the low resistive state (LRS) is caused by the formation of (i) conductive filaments (during the electro-migration of oxygen vacancies); or (ii) conductive metal bridges (during the migration of metal cations) in the oxide matrix, closing the contacts of the MOM structure; or (iii) suppressing (bypassing) the Schottky barrier at one of the structure electrodes. The latter is usually formed using semiconductor oxides with a band gap of $\leq$ 3 eV. When the voltage polarity is reversed, the filament (bridge) is destroyed and a reversible RS to the high resistance state (HRS) is observed in the structure. For stable operation of anionic (with a change of valence) or cationic memristive MOM structures the electroforming process at high voltages is usually required for the first filaments (bridges) formation. However, other RS mechanisms, which do not require electroforming, are possible, such as the recharge of localized electronic states in the Schottky barrier region and/or in the oxide volume (see [16, 17] and Refs. therein), electric repolarization of ferroelectric oxide [18–20], redox reactions in organic materials [21], electron drag effect of metal atoms [22] and, finally, temperature-induced metal-insulator transition in Mott materials (NbO$_2$, VO$_2$, V$_2$O$_3$), which, although was discovered relatively long ago, is still the subject of discussion and studies [8, 23].

Despite the considerable amount of accumulated experimental results, there is still no microscopic theory of reversible RSs. In particular, this is due to the difficulties in describing the interrelated non-equilibrium processes of thermal, electronic, and ion transport in nanometer scale, as well as due to the participation of several RS channels associated, for example, with the simultaneous manifestation of cationic and anionic transport [14] or with the synergetic contributions to RS of ion transport and electric polarization of ferroelectrics [20].
In recent years considerable attention has been paid to the study of phenomena that can accompany the effects of RS in the MOM structures and clearly reflect their features. Such phenomena include: integer (multiple $G_0$) and/or half-integer ($G_0/2$) quantization of the structure conductance at room temperature ($G_0 = 2e^2/h$, where $e$ is the electron charge, and $h$ is Planck's constant) [24-26], and also the change (switching) of its capacity $C$ during the RS [16, 17, 27–32].

The currently known capacitive switching (CS) mechanisms can be divided into two types. The first of them is related to the recharging of traps and/or movement of oxygen vacancies in the Schottky barrier region, which change its size and, accordingly, the capacity of MOM structure [16, 17, 27]. The other is due to the formation (destruction) of the filament percolation network during the movement of vacancies, which changes the effective permittivity and resistance of the MOM structure [28–32]. In the first case, the capacitance change during RS can be significant and exceed 10 times [16, 27]. The work [16] reports as high as a 100-fold change in the capacity of the Au/DyMnO$_3$/Nb:SrTiO$_3$/Au structures under RS. However, such a strong CS, apparently, is entirely due to the introduction into the MOM active region of the DyMnO$_3$/Nb:SrTiO$_3$ heterojunction structure, which has a large capacity. The change in the Schottky barrier capacity at the Nb:SrTiO$_3$/Au interface at RS does not exceed 3 times (see inset to Fig. 2c in [16]). Under the second mechanism, $C$ variation typically does not exceed 3–4 times, and the effects of CS and RS in this case can be both correlated (signs of change of $C$ and $R$ are the same) [29–31], and anticorrelated [28, 32] (in [31] at large $R \geq 10^4 \, \Omega$ growth of $C$ is followed by a fall).

Recently, we have revealed significant effects of RS in metal/nanocomposite/metal (M/NC/M) structures based on a (Co$_{40}$Fe$_{40}$B$_{20}$)$_x$(LiNbO$_3$)$_{100-x}$ NC consisting of 2–3 nm CoFe nanogranules in the amorphous nonstoichiometric LiNbO$_{3-y}$ matrix with a high content of dispersed Fe$^{2+}$ and Co$^{2+}$ magnetic ions, up to (2-3)$\times$10$^{22}$ cm$^{-3}$ [33, 34]. At $x \sim 10$ at. % the number of stable RS cycles exceeded $10^5$ with the ratio of resistance in high-resistance state to that in low-resistance state $R_{on}/R_{off} \sim 50$ [33]. Presumably, the observed effects of RS are associated with the local injection (or extraction) of oxygen vacancies (depending on the voltage sign) into a strongly oxidized NC layer near the electrode of the structure controlling its resistance. Regions of local injection are defined by the positions of percolation chains of granules surrounded by vacancies and/or cations [33] ("metallized" granular chains), which do not change in the process of RS, thus ensuring their high stability. It would seem that under these conditions the CS effect cannot be any significant in terms of the formation of a single injection region. In fact, it turned out that changes in the capacity of M/NC/M structures can reach 8 times during the RS process. The observed effect of CS under RS conditions is explained by the formation of numerous nanocapacitors near the bottom electrode of the M/NC/M structure, with upper plates determined by the position of metallized granular chains, and by a layer of amorphous/nanocrystalline LiNbO$_3$, whose permittivity reaches
The movement of vacancies/cations to the bottom electrode leads to a decrease in the effective thickness of the layer and, as a consequence, to a significant increase in the structure capacity and a decrease in resistance.

II. SAMPLES AND EXPERIMENTAL DETAILS

M/NC/M structures based on the \((Co_{40}Fe_{40}B_{20})_x(LiNbO_3)_{100-x}\) NC are synthesized by ion-beam sputtering using a composite target consisting of cast alloy \(Co_{40}Fe_{40}B_{20}\) plate and 14–15 strips of ferroelectric \(LiNbO_3\) (see details in [29]). An elongated rectangular target with a non-uniform arrangement of \(LiNbO_3\) strips was used, allowing the formation of NC with different concentration of the metal phase in the range of \(x = 6–43\) at. % in a single cycle of synthesis. NC was deposited in the argon atmosphere \((P_{Ar} \approx 8 \cdot 10^{-4}\) Torr) at room temperature on the glassceramic substrates. At the initial stage, the deposition was performed in the mode of a given oxygen flow at its increased partial pressure \(P_{O_2} \approx 2.1 \cdot 10^{-5}\) Torr for 8 min, after which the flow of \(O_2\) was decreased. Further deposition was carried out for 120 min at an average pressure of \(P_{O_2} \approx 1.4 \cdot 10^{-5}\) Torr \((P_{O_2}\) values are given for the chamber vacuum limit \(P \approx 6 \cdot 10^{-6}\) Torr). The thickness of the NC layer in the structures was \(d \approx 1.5\) µm. The electrodes of the structures were made of three-layer Cr/Cu/Cr metal film with a thickness of \(\approx 1\) µm (top electrode size was \(S = 0.5 \times 0.2\) mm²).

It should be noted that the above formula for the NC was used by us to find \(x\) according to the data of energy-dispersive X-ray (EDX) microanalysis [33]. In fact, a significant part of boron appears in the insulating matrix, outside the granules, in the process of synthesis of the NC [33, 36]. At the same time, it is impossible to determine which part of boron remains in the granules by the existing EDX spectroscopy methods. Therefore, following [33], we will use the NC formula notation, reflecting the composition of the target, denoting it for short as \((CoFeB)_x(LiNbO_3)_{100-x}\).

The microstructure of the NC films were studied by high-resolution transmission and scanning transmission electron microscopy (TEM and STEM, respectively) using a TITAN 80-300 TEM/STEM instrument (ThermoFisher Scientific, USA) operating at an accelerating voltage of \(U = 300\) kV, equipped with a Cs-probe corrector, high-angle annular dark-field detector (HAADF) (Fischione, US) and EDX microanalysis spectrometer (EDAX, USA). For the image processing Digital Micrograph (Gatan, USA) software and TIA (ThermoFisher Scientific, USA) were used. Details of preparation of samples for structural studies with atomic resolution are described in [36].

The capacitance of the structures was measured with the help of the HP 4192A impedance analyzer in the frequency range \(f\) from 5 Hz to 13 MHz at amplitude of an alternating signal of 50 mV. Investigations of the electrophysical properties of the M/NC/M structures at DC, including measurements of their I–V characteristics, were carried out with the help of a four-channel source measure unit PXIe-4140 (National Instruments) using the analytical probe station PM5 (Cascade...
Microtech). In the study of the I–V curves, current $I$ was measured with the grounded bottom electrode of the structure and with the alternating voltage $U$ applied to the top electrode according to the linear law in the sequence from $0 \rightarrow + U_0 \rightarrow - U_0 \rightarrow 0$ V with the step of 0.1 V and the amplitude of saw-tooth sweep up to $U_0 = 15$ V. In addition, we studied the temperature dependence of both the I–V characteristics of these structures and their conductance in the relatively weak fields ($\leq 10^3$ V/cm) in the temperature range of 10–300 K using an evacuated insert, immersed in a liquid-helium Dewar flask.

III. RESULTS AND DISCUSSION

A. Conductance of the M/NC/M sandwiches vs metal content and their resistive switching

Fig. 1 shows the dependence of the conductance of the studied structures $G(x) = I/U$ on the metal content measured at DC at $U = 0.3$ V, after action to the saw-tooth voltage with the amplitude up to $U_0 = 3–5$ V, which is insufficient for RS of the structures to the LRS ($U_{LRS} \approx 10$ V; see the inset to Fig. 1). At the same time, however, a significant increase in the stability and reproducibility of the measured value $G$ was provided. The dependence of $G(x)$ is typical for percolation granular systems [37]: below some threshold value $x < x_p$ (percolation threshold; in our case $x_p \approx 17$ at. %) the function $G(x)$ is exponential, and above it $G(x)$ practically does not depend on $x$.

![Graph showing the dependence of conductance $G(x)$ on the metal content $x$](image)

**Fig. 1.** The dependence of conductance $G(x) = I/U$ of the M/(CoFeB)$_x$(LiNbO$_3$)$_{100-x}$/M structures on the metal content $x$, measured at DC at $U = 0.3$ V. The inset shows the I-V curves for the M/NC/M structure with optimal content of $x_{opt} \approx 15$ at. % (the arrows show the voltage scanning direction).
According to our recent studies [33, 38], the strongest and most stable RS in the \(\text{M/(CoFeB)}_{1-x} (\text{LiNbO}_3)_{100-x} /\text{M}\) structures is observed at some optimal content of metal \(x_{opt}\) below the percolation threshold. The specific value of \(x_{opt}\) may depend on the size of the granules and the anisotropy of their shape (elongation along the NC growth axis). In the synthesized M/NC/M structures, the maximum \(R_{off}/R_{on} \sim 40\) ratio is observed at the \(x_{opt}\) value of about 15 at. % (see I–V curves in the inset to Fig. 1), which is close to the \(x_{opt}\) value of 11 at. % obtained for M/NC/M structures with \(R_{off}/R_{on} \sim 50\) and strongly elongated granules (up to 10 nm with lateral sizes of 2-4 nm) [33, 38]. However, the switching voltage \(U_{LRS} \approx 10\) V was almost 3 times higher than in the case of the structures studied in [33, 38]. This fact can be explained by a thicker oxide layer formed at the bottom electrode, as well as with a rounded shape of granules.

Note that the studies of cyclic RSs of the structures were performed at rather large compliance currents \(I_c = 50\) mA (see the inset to Fig. 1); in our previous studies [33, 38] these currents reached \(I_c = 100\) mA. If we assume that this current flows through a single granular metallized chain (MC), the lateral size of which slightly exceeds the diameter of granules and is \(~10\) nm, as for the filaments of most memristors [12–14, 31], the current density would reach about \(10^{11}\) A/cm\(^2\). This is a huge value compared to the limiting current (\(~10^7\) A/cm\(^2\)), which the metal can withstand without destruction due to, for example, the effect of “electron wind” [22]. It follows that at RS of the M/NC/M structure to the LRS, its conductance is determined by many MCs (\(\geq 10^5\)).

**B. Microstructure of the M/NC/M sandwiches with resistive switching effect**

The bright field STEM images of the M/NC/M sandwich with optimal value \(x_{opt} \approx 15\) at.% at different magnifications are shown in Fig. 2a. The CoFe nanogranules embedded in LiNbO\(_3\) layer are sandwiched between Cr/Cu/Cr layers. Close inspection of the interface between the upper Cr layer of the bottom electrode and LiNbO\(_3\) with CoFe nanogranules (marked as CoFe-LiNbO\(_3\)) revealed an amorphous layer with the thickness of 10-17 nm. The enlarged HAADF STEM image of this area is presented in Fig. 2b. The EDX microanalysis unambiguously demonstrated 25 at.% of Nb and 75 at.% of O stoichiometry in this amorphous layer so the layer exhibits dark contrast in Fig.2b. Of course, Li cannot be detected by EDX microanalysis. The results of elemental scan along the red line (from top to bottom) are shown in Fig 2c. The interface between the bottom electrode Cr layer and LiNbO\(_3\) is relatively abrupt, the interdiffusion was not observed. The bottom part of composite CoFe-LiNbO\(_3\) layer consists of CoFe granules, which are approximately 7 nm in size and are slightly larger than the ones in the upper part of the layer. That part of the layer turns out to be a nanocrystal layer with a homogeneous distribution of CoFe nanogranules with the size of 3 nm. The high resolution (HR) TEM image (Fig. 2d) demonstrated that LiNbO\(_3\) matrix is amorphous and CoFe nanogranules are crystalline. The HRTEM image of CoFe granule in [001] zone axis is shown
in the insert to Fig. 2d. This and other images together with Fast Fourier spectra indicated that CoFe nanogranules have a bcc crystal structure with lattice parameter \( a = 0.29 \) nm. The \{110\} crystal planes of bcc lattice are clearly visible with interplanar distance of \(~0.21\) nm.

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![Image](image-url)

Fig. 2. The cross-section image and results of EDX analysis of M/NC/M sample with optimal value \( x_{\text{opt}} \approx 15 \) at. \%. (a) Bright field STEM image of the sample. (b) Enlarged HAADF STEM image of the bottom Cr/CoFe-LiNbO\(_3\) interface. The red line demonstrates the area of EDX element analysis, shown in (c). (d) HRTEM image of the same interface; the inset shows the image of the crystal lattice of the CoFe nanogranule in [001] zone axis.

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C. Behavior of the M/NC/M structures capacity in different resistive states

Fig. 3 shows a typical impedance hodograph (Cole–Cole plot), i.e. the dependence of the imaginary part of impedance \( Z' \) on the real one \( Z'' \), which was obtained for \( M/(CoFeB)_{x}(LiNbO_3)_{100-x}/M \) structure with \( x \approx 16 \) at. \% in the HRS. The inset to Fig. 3 also shows the dependence of \( Z''(Z') \), obtained for the same structure in the LRS. Similar dependencies were observed for all the M/NC/M structures with different content of metal phase. Note, that the hodographs obtained for the HRS and LRS look like semi-circles.
Fig. 3. The dependences of the imaginary part of the impedance on the real one for the M/NC/M structure with $x \approx 16$ at. % in the HRS and LRS (the top inset). The bottom inset shows the equivalent circuit of the M/NC/M structure (explanations are given in the text).

According to the qualitative model of RS proposed in [33], to describe these dependencies it would be necessary to use an equivalent electrical scheme (see the bottom inset in Fig. 3), consisting of a parallel $R_sC_s$ circuit and a resistance $R_c$ connected to it in series, which are shunted by a parallel connected geometric capacitance $C_g^*$ of the M/NC/M structure, modified because of the presence of metallic nanoparticles in the dielectric. The resistance $R_s$ and the capacitance $C_s$ are naturally related to the presence of a high-resistance layer near the bottom electrode of the structure, which determines its switching from one resistive state to another. The resistance $R_c$, in turn, is related to the resistance of the granulated MCs, providing contact of the $R_sC_s$ circuit with the top electrode of the structure. It is obvious that the resistance $R_c$ is much lower than the resistance of the switching layer $R_s$ in the HRS of the memristor.

It is known that an equivalent circuit, similar to that described above, should in general lead to two semi-circles on the hodograph [39]. However, this is not observed in our experiments because the time constant $R_cC_g^* \leq 10^{-8}$ s (see below) is rather small and lies far beyond the range of
relaxation times \((1/f \approx 10^{-7} \text{ s})\). Therefore, the hodographs shown in Fig. 3 are described quite satisfactorily by the separate \(R_sC_s\) circuits (corresponding curves are shown in solid lines in Fig. 3).

It should be noted that the centers of the semi-circles of impedance hodographs do not lie on the axis of the real \(\text{Re}(Z)\) impedance, but are below it. This fact may be related to the presence of some distributed elements in the nanocomposite/high impedance layer/electrode system. This leads to the conclusion that the relaxation time \(\tau\) is not a constant value, but is continuously or discretely distributed with respect to its mean value [39].

In this situation, we should expect a fairly strong dependence of the measured capacitance on the frequency \(C(f)\). In Fig. 4 the dependencies of \(C(f)\) in the HRS and LRS of the structure on the alternating signal frequency for a sample with \(x \approx 14\) at. % are shown. As can be seen from the figure, the capacitance of the structure decreases in both cases with increasing the frequency. Meanwhile at high frequencies \((f \approx 10^7 \text{ Hz})\) the capacitances in the HRS and LRS practically coincide. Similar dependencies of \(C(f)\) were obtained for the other samples studied. It is necessary to note that the resistances \(R_{HF}\) in the HRS and LRS at the high frequency of \(f \approx 10^7 \text{ Hz}\) also coincide (see the inset to Fig. 4). And, according to the equivalent scheme (Fig. 3), \(R_c \sim R_{HF} \sim 100 \Omega\). In addition, note that the structure resistance, when below the percolation threshold,
real part of the conductance practically does not depend on the frequency up to \( f \sim 10^4 \) Hz (see, for example, [40]).

A significant decrease in capacitance can be attributed both to a decrease in the permittivity of the amorphous \( \text{LiNbO}_3 \) matrix with an increase in the frequency of the alternating signal [35] and to the shunting effect of the effective geometric capacitance \( C_g^* \) of the M/NC/M structure, which can be significantly increased due to the presence of metallic nanoparticles in the dielectric matrix. In the Maxwell-Garnett approximation, which is valid for a small volume fraction of spherical nanoparticles \( x_v \ll 1 \), the complex effective permittivity of the composite medium is determined by the expression [41]:

\[
\varepsilon_{\text{eff}} = \varepsilon_{\text{MG}} = \varepsilon_d + 2\varepsilon_d \varepsilon_m + 2x_v(\varepsilon_m - \varepsilon_d) \varepsilon_{\text{eff}} - x_v(\varepsilon_m - \varepsilon_d),
\]

where \( \varepsilon_d \) and \( \varepsilon_m \) are permittivity of the dielectric and metal, respectively. Considering, as usual, that for metal the imaginary part of the permittivity \( \text{Im}(\varepsilon_m) \) is much larger than its real part \( \text{Re}(\varepsilon_m) \) and also much larger than the permittivity of the dielectric \( \varepsilon_d \), which is obviously fulfilled up to high frequencies, we obtain that the real part of the effective permittivity of the composite medium is equal to:

\[
\varepsilon_{\text{eff}} = \text{Re} \varepsilon_{\text{MG}} \approx \varepsilon_d (1 + 3x_v).
\]

The equivalent circuit in Fig. 3 shows that when the capacitance values in the HRS and LRS are close, the capacitance measured is defined as:

\[
C \approx C_g^* \approx C_g(1 + 3x_v) = \frac{\varepsilon_d S}{4\pi d}(1 + 3x_v),
\]

where \( C_g \) is the geometric capacitance of the structure in the absence of metallic nanoparticles in the dielectric. At \( x \approx 14 \) at. \% the volume fraction of metal \( x_v \approx 8 \) vol. \% for the \( \text{(CoFeB)}_x(\text{LiNbO}_3)_{100-x} \) NC. Taking this into account, substituting the nominal value of \( \varepsilon_d \approx 50 \) [35] in (3), we obtain \( C \approx 40 \) pF, which is close to the experimentally measured value of \( C \approx 60 \) pF (Fig. 4). It should be noted here that the elongation and/or short-circuit of the granules along the growth axis of the NC can strongly increase their polarizability and the total capacity of the structure. In a more general case, for ellipsoidal granules: \( \varepsilon_{\text{eff}} \approx \varepsilon_d (1 + x_v / L) \), where \( L \) is a form-factor less than \( 1/3 \) for oblong ellipsoid \( (L = 1/3 \) for the sphere). The experimentally found value of \( C = C_g^* \approx 60 \) pF corresponds to the form-factor \( L \sim 0.1 \), inherent in the granules in the shape of prolate ellipsoid of revolution with the long to short axis ratio of \( \sim 3 \). Note that in our case \( R_{\text{f,pp}} C_g^* \sim 10^{-8} \) s, which is much less than \( 1/f \).
The switching of the M/NC/M structure to the LRS should be accompanied by a reduction in the thickness of the high-resistance layer, which in turn should lead to an increase in capacitance. This effect, obviously, should be the stronger the greater the \( R_{\text{off}} / R_{\text{on}} \) ratio, which is quite clearly manifested in our case in the study of correlation between the relative change in resistance and capacitance in the structures with different metal content (Fig. 5). The maximum relative capacitance change of up to 8 times, as well as the maximum relative resistance change (about 40 times), is observed below the percolation threshold for the structures with \( x \approx 14–16 \) at. %.

![Fig. 5. Dependence of the relative change in resistance and capacity of the M/NC/M structure during its RS between the HRS and LRS on the content of metallic nanoparticles at a frequency of 1 kHz.](image)

A fairly significant change in \( C \) during RS with formation of metal filaments was observed in [31, 32], where capacity variations reached 3–4 times. Apparently, the multifilament mechanism of RS close to our case was realized in [31]. At the same time, in [31] the capacitance at first slightly increased with decreasing resistance, and then strongly (4 times) fell, which was associated with the formation of solid (without ruptures) metal Ni bridges. In our case, when the resistance decreases, the capacitance experiences only growth.

**D. Qualitative model of resistive/capacitive switching**

Let one consider a possible multifilament mechanism of RS in our case, taking into account: (i) the high content of dispersed Co and Fe atoms in the insulating LiNbO$_3$–y matrix (up to \( \sim 3\cdot10^{22} \) cm$^{-3}$ [33,34]), and (ii) the presence in the M/NC/M structures the high-resistance layer of amorphous/nanocrystalline LiNbO$_3$ with \( \varepsilon_d \) reaching \( \sim (10^2–10^4) \) [35] which is formed near the bottom electrode during the NC growth under a large excess of oxygen (see Fig. 2b).
Fig. 6 illustrates the qualitative RS model under the above stated conditions. In a pristine state the dispersed atoms are uniformly distributed in the isolating matrix (Fig. 6a). But after applying a voltage and passing a current, the nucleation of dispersed atoms around chains of granules producing percolation paths can occur, and as a consequence the formation of metallized chains or MCs. It is obvious that the manifestation of the nucleation effects is due to the strong oversaturation of the considered system by dispersed atoms and the presence of metallic nuclei (nanoparticles) in it. Previously, similar effects were observed, for example, in SiO₂-based memristive structures with dispersed Pt or W atoms [42, 43].

![Fig. 6. The qualitative model of RS in the M/NC/M structures.](image)

Fig. 6. The qualitative model of RS in the M/NC/M structures. (a) The M/NC/M structure in a pristine state after synthesis. Green color shows amorphous/nanocrystalline LiNbO₃₋ₓ matrix, containing metal CoFe nanogranules (black ovals) and nonequilibrium phase of Co and Fe atoms with a concentration reaching ~10²² cm⁻³ (gray circles). The red lines show the percolation paths that determine the current after applying a voltage to the structure. The green dashed line separates the high resistance layer near the bottom electrode of the structure from predominantly stoichiometric LiNbO₃, in which there is no nonequilibrium atomic metal phase. (b) The M/NC/M structure in HRS after cyclic RS and applying negative potential to the top electrode. The gray areas surrounding the chains of granules are metallic condensate, which occurs due to the nucleation processes of Co and Fe atoms and oxygen vacancies when the current flows through the structure. (c) The M/NC/M structure is in the LRS after applying positive potential above a certain value to the top electrode.

When a sufficiently large negative voltage is applied to the top electrode, the structure switches to the HRS due to the movement of oxygen vacancies (cations) to the top electrode by means of MCs and increasing the effective gap $l_g$ between the MCs and the bottom electrode (Fig. 6b). On the other hand, the capacitance of the structure in this situation must fall, since in a rough approximation the value of $C \propto 1/l_g$. The reverse situation arises when a sufficiently large positive voltage is applied to the structure (Fig. 6c). However, in this case, the migration of vacancies (cations) from MCs to the bottom electrode during switching the structure to the LRS
leads to a reduction of the gap, but not to its complete “collapse”. This is probably due both to the relatively thick oxide layer and to the considerable resistance of MCs, which causes the redistribution of voltage drop between $R_s$ and $R_c$ during switching the structure to the LRS (see Fig. 3) and, as a consequence, the absence of short circuits between the MCs and the bottom electrode.

Simple estimates confirm the reasonableness of the proposed RS model. Assuming $l_g \sim 1$ nm in LRS, $\varepsilon_d \sim 10^3$, lateral MCs size of about 10 nm, and their number $\sim 10^7$ (corresponds to the distance between MCs $\sim 100$ nm), we obtain the structure capacity $C \sim 9000$ pF, which is consistent with the results of the experiment: $C \approx 9000$ pF at $f \approx 400$ Hz (Fig. 4).

**E. Temperature dependencies of resistance**

To obtain further insight into peculiarities of the RS, confirming our model, the temperature dependencies of resistance $R(T)$ were investigated for structure in both the HRS and LRS. Switching to the LRS was carried out at the temperature of 250 K (Fig. 7a) in order to avoid the influence of possible conductance relaxations on the dependence of $R(T)$. Note, that the RSs were not observed below 200 K in the whole voltage range from $-15$ to $+15$ V. Under these conditions the I–V curves were symmetrical and nonlinear (Fig. 7b).

**Fig. 7.** Typical I–V curves measured for the M/(CoFeB)$_x$(LiNbO$_3$)$_{100-x}$/M structure with $x = 15$ at. % at (a) $T = 250$ K and (b) $T = 50, 100$ and 200 K.
Fig. 8 shows the $R(T)$ dependencies in the HRS and after switching the structure to a lower resistance state, as a result of which its resistance decreases by 4 times. In both cases, the activation dependences are observed, moreover, in a wide temperature range ($T = 15–120$ K) they are approximated with high accuracy (better than 1%) by the function $\ln R$ on $(1/T)^{1/2}$. For comparison, the inset to Fig. 8 also shows the dependence of $\ln R$ vs $1/T$, which is not linear in the studied temperature range. In other words, the conductance follows the law of $\ln R \propto (T_0/T)^{1/2}$, often observed in systems with hopping conductivity [33, 44], and with almost identical values of the parameter $T_0 \approx 1440$ K (in HRS) and 1410 K (in LRS). This clearly indicates that in our case RS of the structure to lower resistance state is accompanied by a decrease in the $l_e$ value and absence of metal short circuits. The large value of $T_0$ is obviously related with the large energy depth of traps in the oxide and the strong localization of electrons on them. Indeed, in the case of doped semiconductors (or highly defective dielectrics), the law “1/2” in the $R(T)$ dependence is associated with the formation of a Coulomb gap near the Fermi level. The parameter $T_0$ is determined by the localization radius $a_B$ of the electron at the defect [44]: $k_B T_0 \sim e^2 / \varepsilon_d a_B$, where $k_B$ is Boltzmann's constant, $e$ is the charge of the electron. In the case of the strong localization (of about the lattice constant), the permittivity at optical frequencies should be used to estimate $a_B$, assuming $\varepsilon_d \approx \varepsilon_{opt}$. In LiNbO$_3$ the value of $\varepsilon_{opt}$ is about 10 [45]. Using the expression for $T_0$ and the value found in the experiment of $T_0 \sim 1400$ K, we obtain $a_B \sim 1$ nm, which is a reasonable result (hexagonal lattice parameters for LiNbO$_3$: $a = 0.5148$ nm and $c = 1.3863$ nm [45]).

![Fig. 8. $R(T)$ dependencies in the two different resistive states in coordinates of $\ln R$ vs $(1/T)^{1/2}$. The inset shows $\ln R$ as a function of $1/T$.](image-url)
IV. CONCLUSION

Thus, the experimental results presented above and their analysis show that the originality of the memristive properties of the M/NC/M samples based on the \((\text{Co}_{40}\text{Fe}_{40}\text{B}_{20})_{x}(\text{LiNbO}_3)_{100-x}\) NC is determined both by their structural features associated with the formation of high-resistance and highly polarizable (high-\(\kappa\)) oxide interface layer and by the multifilamentary nature of the resistive switching. The latter is due to the presence of a large number of granules in the oxide matrix as well as dispersed metal atoms in it, whose nucleation causes formation of many channels of resistive switching. As a result of synergetic combination of these factors, not only a significant change in the structure resistance is observed, but also in its capacity, which reaches 8 times at the ratio of \(R_{\text{off}}/R_{\text{on}} \sim 40\). The multifilamentary character of RS, apparently, entirely determines the high level of plasticity of our samples (the possibility of a smooth change of the resistance in the \(R_{\text{on}}-R_{\text{off}}\) window), which, in particular, allows emulating the unique properties of biological synapses using them [46, 47].

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