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Memristor effect in PZT:TiO$_x$ composite film

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The electrical properties of a new type of capacitor structures with a Pt/PZT:TiO$_x$/Pt composite film, in which the three-dimensional nanoscale pore structure in the ferroelectric lead zirconate titanate film is filled with titanium dioxide, are studied. The memristor effect is detected using electrical measurements on direct and alternating current, as well as by measuring the local current using contact atomic force microscopy, which opens up prospects for studying such structures for use in advanced resistive memory devices.

Keywords: ferroelectric composite film, titanium dioxide, switchable resistive states.

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The memristor effect of reversible resistance change in metal–insulator–metal structures is the basis of resistive memory (ReRAM), which is one of the most promising classes of non-volatile memory devices. The great interest of the semiconductor industry in this type of memory is attributable to the potential to obtain such speed and resource characteristics that exceed the current level of 3D NAND devices, its compatibility with the low-temperature metallization process, and the possibility to implement a crossbar architecture and neuromorphic computing [1,2]. However, despite extensive research, a rather modest level of integration has been achieved to date, which is due to an insufficient operating life, memory window instability, and other problems caused by the stochastic nature of the formation and destruction of conductive filaments [2]. One of the approaches being developed to increasing the stability of switching processes is the intentional introduction of defects into the structure (e.g., porous materials), which leads to modulation of local electric fields and stabilization of switching processes [3–5]. The present study is the first to investigate the possible manifestation of the memristor effect in a fundamentally new material: a porous film with a three-dimensional interconnected system of nanoscale channels made of titanium oxide, which is known for its memristor properties. A ferroelectric, lead zirconate titanate (PZT), was chosen as the matrix material, which may provide additional control over the device parameters.

The method of formation of PZT:TiO$_x$ composite structures was detailed in [6]. Silicon wafers with the Si/SiO$_2$/Ti/Pt structure served as substrates. The sol-gel process of molecular self-assembly was used to form porous Pb(Zr$_{0.48}$,Ti$_{0.52}$)O$_3$ films [7]. The resulting films had a thickness of 315 nm, a perovskite structure with columnar grains 0.6–6.2 μm in size, and a three-dimensional system of channel-shaped pores with a diameter of $\sim$ 20 nm. The TiO$_x$ phase was introduced by the atomic layer deposition method, which ensured conformal penetration of the material throughout the entire volume of the porous film with TiO$_x$ deposited onto the pore walls in an amorphous phase. The resulting volume fraction of TiO$_x$ was 7 % of the volume of the PZT film, and the film thickness on the PZT surface was $\sim$ 10 nm. The top Pt electrodes with a thickness of 10 nm and an area of $S \sim 10^{-3}$ cm^2 were deposited by magnetron sputtering. When electrical measurements were conducted, probes were lowered onto the top and bottom Pt contacts under a microscope to connect the sample to the measurement circuit. The top contact was grounded, and a voltage was supplied through the probe to the bottom

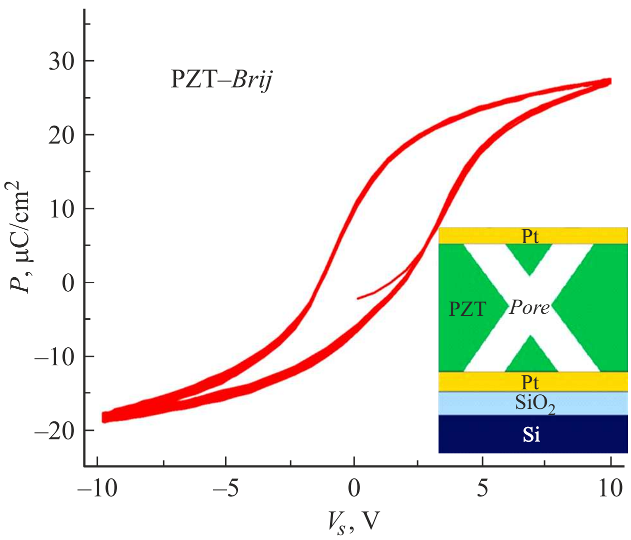

Figure 1. The dependence of the polarization on the structure voltage measured in the Sawyer–Tower circuit within ten sinusoidal periods. The inset shows the sketch of the empty-pore PZT structure in which pores were formed using the Brij76 porogen.

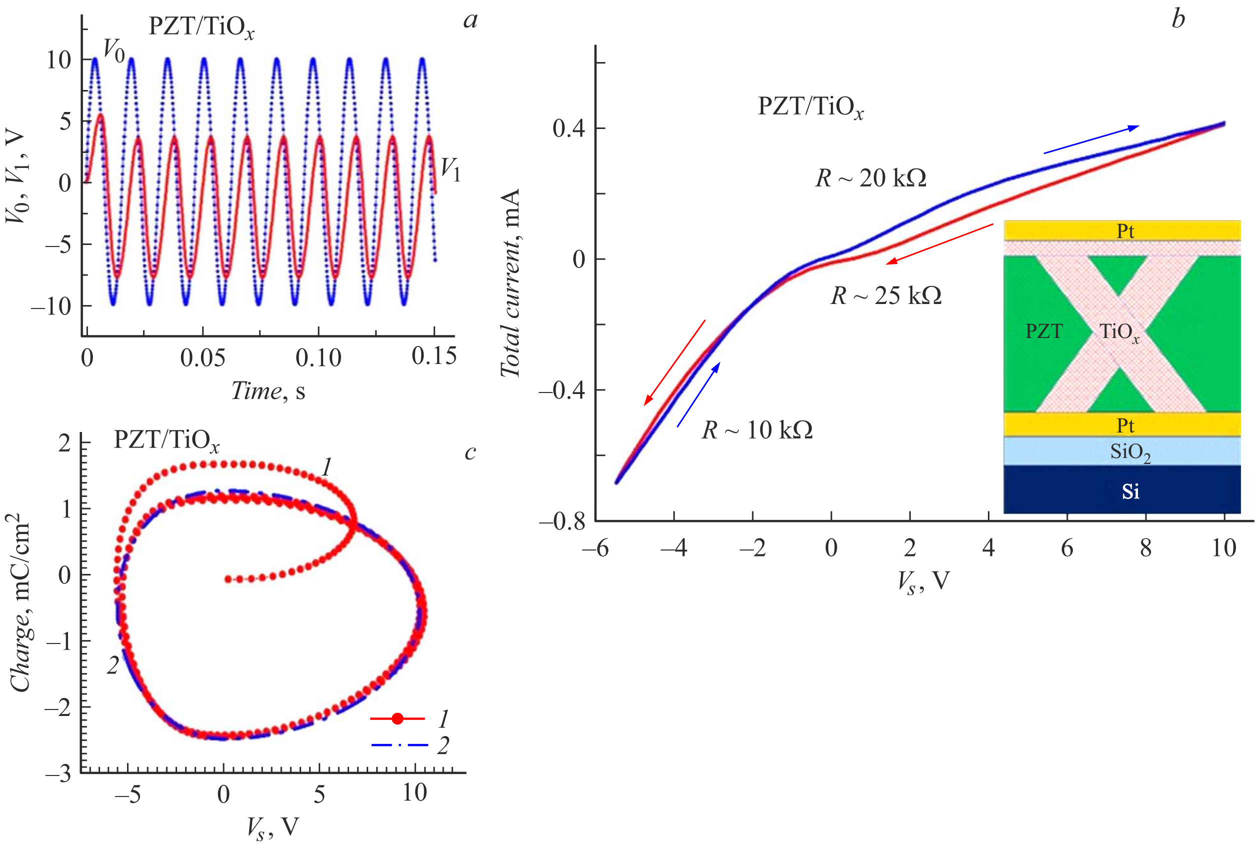

Figure 2. PZT with TiO$_x$ in pores. The polarization measurement in the Sawyer–Tower circuit: *a* — time dependences of the input V_0 and the output V_1 voltages; *b* — the dependence of the total current through the structure on the voltage across it within a single sinusoidal period (the structure with TiO$_x$ in pores is shown in the inset); and *c* — variation of the charge at the top electrode of the Pt/PZT/TiO$_x$/Pt structure with the sample voltage (*1* — measured; *2* — calculated for the *RC* circuit).

electrode. Current–voltage curves (CVCs) were examined using a 6487 Picoammeter/Voltage Source (Keithley).

Three types of experiments were performed. First, a Sawyer–Tower circuit was used to measure the film polarization and the flowing current. In this case, the input sinusoidal voltage V_0 with a frequency of 64 Hz was applied to the series connection of the sample and the reference capacitance, the value of which $C_{et} = 220$ nF is much greater than the sample capacitance (~ 3 nF) and therefore does not affect the magnitude of the flowing current. At the same time, the output voltage V_1 was taken from the reference capacitor. The polarization P (i.e., the charge Q per unit area of the top electrode of the structure) was calculated as $P = Q/S = C_{et}V_1/S$, and the current was determined as $I = C_{et}dV_1/dt$. The results of the polarization calculation P for a film with empty pores are presented in Fig. 1. The sketch of the PZT structure with empty pores is shown in the inset. Despite the presence of pores, the PZT film retains polarization properties, but with a lower remnant polarization value; the current through the structure is essentially capacitive and does not exceed 30 μA.

A completely different pattern is seen for the PZT:TiO$_x$ structure (inset in Fig. 2). The amplitude of oscillations V_1 increases by more than an order of magnitude, a strong asymmetry of the voltage response V_1 to the polarity of the input voltage V_0 is observed (Fig. 2, *a*), the current increases by an order of magnitude, and the dependence of the current on the structure voltage $V_s = V_0 - V_1$ turns out to be close to a resistive one (Fig. 2, *b*) with average resistance values of 22 and 10 kΩ at the positive and negative voltage, respectively. The dependence of the charge Q at the top electrode of the structure on the voltage (curve *1* in Fig. 2, *c*) is typical of a circuit consisting of a series-connected resistance and capacitance C_{et}. Moreover, if we substitute the structure under consideration with the resistances indicated above and neglect the intrinsic capacitance of the film, the dependence $Q(V_s)$ (curve *2* in Fig. 2, *c*), which is almost a perfect match to experimental curve *1* in Fig. 2, *c*, is obtained. This suggests that the current mainly flows through the pores filled with the TiO$_x$ phase, which is in the conducting state, and the contribution of the capacitive current associated with the polarization charge is quite small. In addition, the current–voltage curve in Fig. 2, *b* has the form of a hysteresis loop with its branches intersecting in the vicinity of zero, just as in the memristor structures Pt/TiO$_2$/Pt [8], which indicates the existence of two resistive states. However, the „window" between the branches is rather narrow; therefore, these

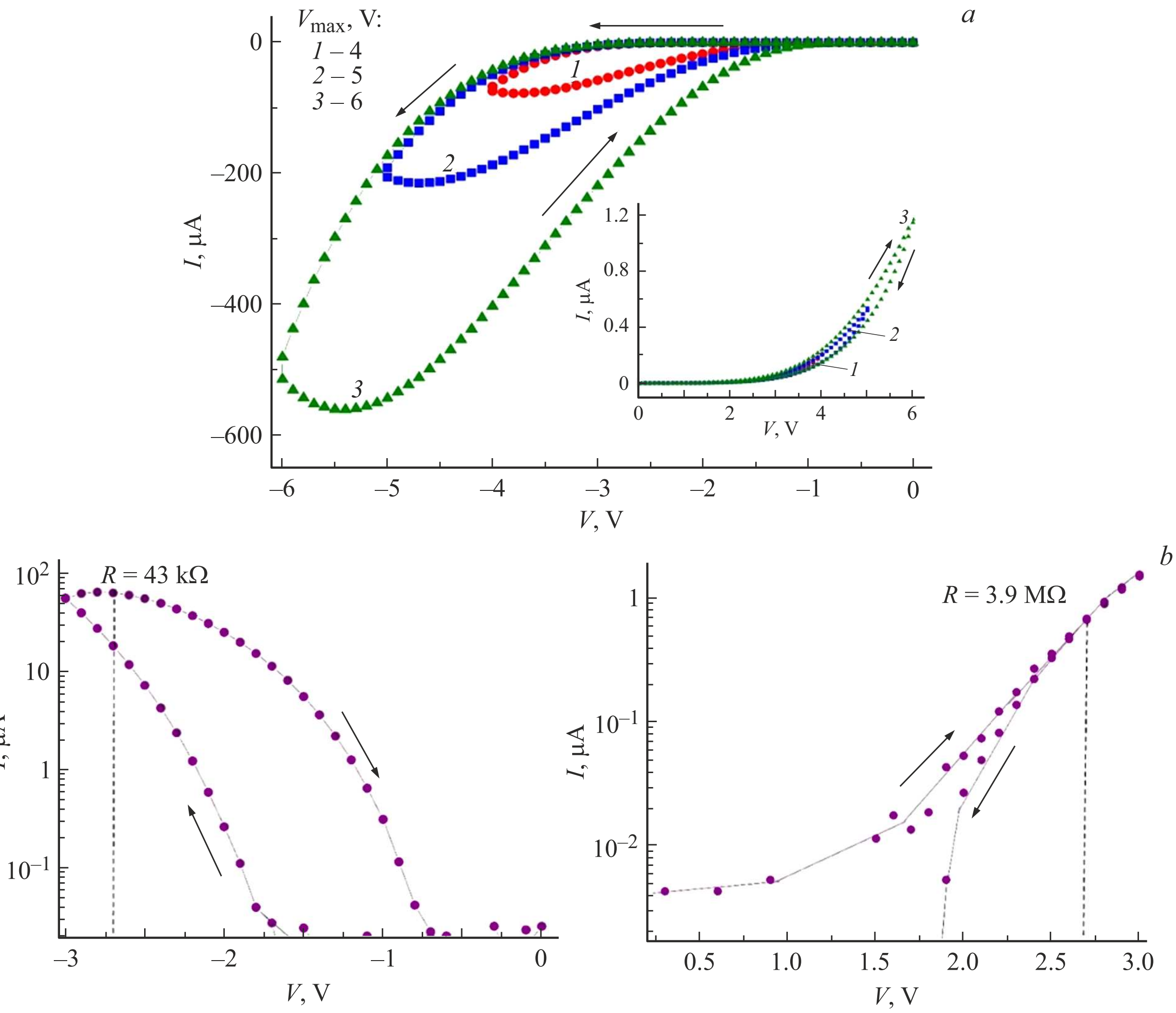

Figure 3. CVCs of the PZT:TiO_x structures measured in the initially depolarized films: *a* — in the $0 \to -V_{max} \to +V_{max} \to 0$ mode for $V_{max} = 4$ (*1*), 5 (*2*), and 6 V (*3*) with the data presented on a linear scale for $V < 0$ and $V > 0$ (inset); *b* — in the $0 \to +V_{max} \to -V_{max} \to 0$ mode for $V_{max} = 3$ V with the data presented on a logarithmic scale. The resistance values at voltages of -2.7 and $+2.7$ V are indicated.

states differ little from each other. It may be assumed that this is attributable to a large PZT/TiO_x interface area, but further research is actually needed to explain this fact.

In the second group of experiments, DC CVCs were measured by applying a sequence of voltage steps with a height of 0.1 V and a duration of 0.2 s in the $0 \to -V_{max} \to +V_{max} \to 0$ or $0 \to +V_{max} \to -V_{max} \to 0$ mode; the direction from the bottom electrode to the top one was considered positive. The series resistance of the circuit was zero in CVC measurements. The empty-pore PZT structure has a typical CVC with a current value below 1.5 nA and a clockwise current hysteresis in any bias direction, while PZT with TiO_x in its pores features an asymmetric (depending on the voltage polarity) behavior of current and two resistive states at $V < 0$ (Fig. 3, *a*) and $V > 0$ (inset of Fig. 3, *a*). Note that the width of the „window“ between the current branches is ~ 2.5 V at negative voltages and near-zero at positive voltages. Figure 3, *b* shows the resistance estimates obtained at $V = \pm 2.7$ V. They differ by a factor of 90, indicating the existence of resistive states with low and high resistance values. Thus, a reversible resistive switching of the structure resistance is observed under the influence of the applied voltage, which characterizes the memristor effect [9]. Note that the resistance at a near-zero bias voltage is fairly high (due possibly to the presence of back-to-back Schottky barriers).

In the next series of experiments, local current mapping was performed using conductive atomic force microscopy (C-AFM). This technique enables the simultaneous acquisition of two-dimensional topographical images and corresponding spatial maps of the local current flowing between the probe and the bottom electrode during surface scanning. The measurements were conducted using probes with a

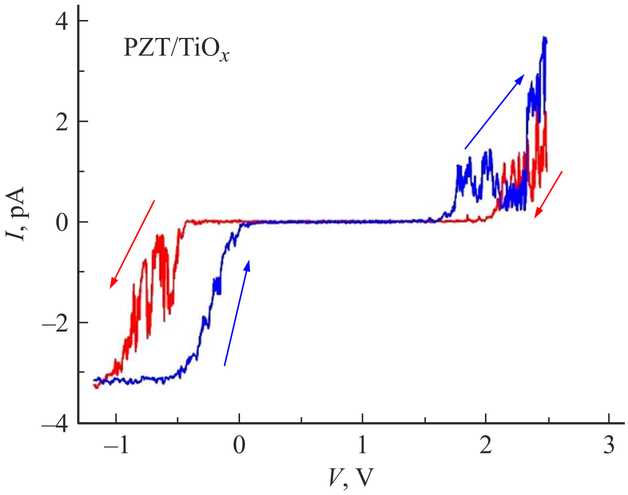

Figure 4. CVCs of PZT:TiO$_x$ structures measured by the contact atomic force microscopy.

conductive Pt coating, featuring a spring constant of 0.5 N/m and a tip curvature radius of 10 nm; the thickness of the Pt layer was 20–30 nm. The experimental noise floor for current detection was 0.05 pA. As anticipated, local currents measured in the PZT film with unfilled pores were negligible, not exceeding 0.5 pA, and exhibited no correlation with the surface topography at applied voltages up to 4 V. In contrast, the incorporation of TiOx into the pores resulted in a significant localization of current flow within these regions. Furthermore, the local current-voltage characteristics (CVC) became asymmetric and exhibited a pronounced hysteresis loop. This loop is a hallmark of the memristor effect, with a switching window width of approximately 0.6 V (Fig. 4).

We have demonstrated earlier that when Pt/PZT/TiO$_x$/Pt structures are irradiated with visible light, a photocurrent is induced [6] by the photoexcitation of electrons from the valence band of TiO$_x$ to the Ti^{3+} levels located near the bottom of the conduction band and their hopping transport along the levels of titanium in the band gap under the influence of the electric field of the bottom Schottky barrier. It is natural to expect that a similar mechanism should also leave a mark on the above CVC measurements. However, in addition to this factor, the electromigration of oxygen vacancies in TiO$_x$ and the polarization charge at the PZT:TiO$_x$ interfaces both near the electrodes and at the pore boundaries may also play a significant part [10]. Even in a depolarized state, a noticeable negative polarization $P_d = -3.3\,\mu$C/cm^2 is indeed found in the film with empty pores (Fig. 1, b), suggesting the presence of a positive polarization that is not switched by the electric field [11]. The presence of a polarization charge at the interfaces with PZT:TiO$_x$ pores will also affect the barrier height of this interface and induce a built-in field inside the pores. It is evident that further research is needed to find an explanation of the observed effect.

Thus, the memristor effect in a capacitor structure with a composite ferroelectric PZT film and a three-dimensional system of nanoscale channels filled with the TiO$_x$ phase has been demonstrated for the first time. There is reason to believe that a structure satisfying up-to-date requirements applicable to resistive memory elements may be obtained by varying the conditions for the formation of the composite film and electrode materials.

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Conflict of interest

The authors declare that they have no conflict of interest.

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