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Energy-efficient and stable resistive switching in vanadium dioxide nanocrystals

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In this work we investigate an electrically-driven semiconductor-metal phase transition in formed polycrystalline films, nanocrystal arrays, and a single nanocrystal of vanadium dioxide. An increase by about an order of magnitude in the current jump during the phase transition was observed in the nanocrystal arrays compared to solid films, which is in agreement with the parallel resistance model. We found that the switching threshold power decreases by 4−5 orders of magnitude when compared a solid film to single nanocrystals and reaches a value of about 40 nW. This effect occurs due to lower heat dissipation in single nanocrystals. Vanadium dioxide nanocrystals have demonstrated high stability when switched at least 10^{10} times. The results obtained are promising for the formation of energy-efficient, stable and durable switching elements based on vanadium dioxide single nanocrystals.

Keywords: vanadium dioxide, semiconductor-metal phase transition, resistive switches, nanostructures, threshold power, switching stability.

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1. Introduction

Currently, there is an active search for new functionally rich materials and structures for the creation of new generation electronic and optical computing devices [1,2]. One of the most promising candidates is vanadium dioxide (VO_2) — a material with an ultrafast (up to 26 fs) [3] reversible semiconductor-metal phase transition occurring at a temperature of $\sim 68\,^{\circ}C$ and accompanied by a change in conductivity by several orders of magnitude [1,4,5]. The unique properties of VO_2 make it a promising material for energy-efficient and fast switches used in neuromorphic systems, memory, and other high-speed devices [5–8].

The main attention of researchers is focused on the formation of thin polycrystalline films of VO_2, which is attributable to the relative simplicity and low cost of synthesis technology [9]. However, the use of polycrystalline films in commercial devices is seriously limited due to the structural phase transition from a monoclinic lattice (in the semiconductor state) to a tetragonal lattice (in the metallic state). During the structural transition, the lattice constant changes by 1 %, which leads to significant mechanical stresses, cracking and degradation of the material during multiple switching cycles [10].

In recent years, methods for creating nanoscale crystals of VO_2 have been actively developing. Reducing the size of the active region and localizing the electric current inside a single nanocrystal can reduce the required energy for the phase transition and increase the stability of the switches [11–14]. However, the synthesis of high-quality nanocrystals VO_2 and the formation of contacts to them remain technologically challenging tasks [15,16]. The question of studying the mechanism of phase transition in a single nanocrystal of VO_2 and determining its parameters also remains open.

In this paper, an electrically initiated phase transition is investigated in formed polycrystalline films, arrays of nanocrystals, and a single nanocrystal of VO_2. The results of a study of the morphology and phase composition of the formed structures are demonstrated, and the main parameters of an electrically initiated phase transition in them are determined. It is shown that the threshold power per resistive switch decreases sequentially during the transition from a solid film of VO_2 to an array of nanocrystals and further to single nanocrystals. The threshold switching power consumed in nanocrystals is 4−5 orders of magnitude less than in solid films due to a decrease in Joule heat dissipation during switching. The results obtained show that resistive switches based on single nanocrystals of VO_2 are promising as energy-efficient, stable and durable elements for neuromorphic system.

2. Experimental procedure

Polycrystalline films VO_2 with a thickness of ~ 200 nm were synthesized on conductive silicon substrates (*n*-Si,

$\rho \approx 0.001-0.005\,\text{Ohm}\cdot\text{cm}$) by chemical vapor deposition (CVD) in a horizontal reactor with hot walls, detailed synthesis conditions are described in Ref. [17]. Arrays of single nanocrystals of VO_2 were formed from amorphous films VO_x synthesized on *n*-Si substrates by atomic layer deposition (ALD) followed by annealing at a temperature of 650 °C for 2 h. A detailed analysis of optimal conditions for post-cold annealing of thin amorphous films for the formation of high-quality nanocrystals of VO_2 is described in Ref. [18].

The morphology of the formed structures was studied using scanning electron microscopy (SEM) on a Hitachi SU8220 microscope at electron beam energies of 5 keV.

The formed structures were characterized by X-ray phase analysis on a Bruker D8 diffractometer (source — Cu$K\alpha$, detector —LYNXEYE XE-T, range 2θ angles — 5–65°, step — 0.03°, accumulation time — 5 s per measurement). The obtained diffractograms were analyzed in accordance with the PDF file catalog [19].

Temperature measurements of resistance were carried out in the range of 20–80 °C for all synthesized samples. A resistance jump of more than 3 orders of magnitude caused by the semiconductor-metal phase transition in the VO_2 M-phase was detected at a temperature of 65–70 °C.

Electrical measurements of the samples were performed using a Keysight 34461A measuring instrument in the range from 0 to 5 V with a current limit of 1 mA. The conductive substrate *n*-Si acted as a single contact. The second contact was a tungsten needle with a radius of curvature of several tens of micrometers, which can be considered as a flat pressure contact, due to the fact that its radius of curvature is much larger than the average size of crystallites of VO_2 (~ 100 nm).

The electrical characteristics of a single crystal of VO_2 in the temperature range from 20 to 70 °C with the increments of 5 °C were measured using atomic force microscopy(AFM) with a conductive probe on the NTEGRA AURA microscope (NT-MDT). Commercially available conductive AFM needles with a radius of curvature of ~ 35 nm (NT-MDT) were used as one of the electrical contacts, a conductive substrate of *n*-Si was the second contact. The contact area of the AFM needle with the measured nanocrystals will range from 10 to 500 nm^2 [20].

Electrical characteristics were measured in a pulsed mode to test the formed films and crystals of VO_2 for stability during multiple resistive switching. A triangular signal with a frequency of 100 kHz was applied to the structure in the voltage range from 0 to 3 V with a current limit of 1 mA. 10^{10} resistive switching cycles were performed.

3. Experimental results and discussion

As a result of synthesis by CVD methods, polycrystalline films with a thickness of ~ 200 nm, which have a pronounced polycrystalline surface morphology (see *Appendix*, Figure A.1, *a*).

Arrays of VO_2 nanocrystals were obtained as a result of temperature annealing of amorphous films VO_x. The initial ALD of amorphous films VO_x contain vanadium with oxidation states of +4 and +5 and have a resistance of ~ 10 MOhm. Such films VO_x crystallize as a result of annealing and disintegrate into arrays of single nanocrystals (see *Appendix*, Figure A.1, *b*). The percentage of crystals covering the substrate surface is 40–80 %, their average height is 150–200 nm, and the lateral size is 300–400 nm.

As a result of diffraction measurements of the nanocrystal array, it was found that all synthesized structures contain predominantly peaks of VO_2 M1 (001) and VO_2 M1 (002), which indicates a significant predominance of the crystalline phase of VO_2 M1 in nanocrystals (see *Appendix*, Figure A.2, *a*).

For arrays of nanocrystals of VO_2, the dependence of resistance on temperature was measured in the range of 20–80 °C. It was found that at a temperature of 66 °C, a semiconductor-metal phase transition occurs with a sharp decrease in resistance of $\sim 10^3$ times (see *Appendix*, Figure A.2, *b*). This magnitude of the resistance jump confirms the predominance of VO_2 M-phases in the obtained structures, which is consistent with the results of X-ray phase analysis.

As a result of measurements of electrical characteristics in the voltage source mode, current-voltage dependences were obtained for polycrystalline films of VO_2 and nanocrystal arrays of VO_2 (Figure 1). A current surge of several times was detected on all dependencies, corresponding to a change in resistance during an electrically initiated phase transition (resistive switching). This jump occurs when the threshold voltage U_{tr} and the corresponding current I_{off} are reached, the values of which depend on the geometric dimensions of the structure and the properties of VO_2. The corresponding electrical characteristics in the current source mode are given in *Appendix*, Figure A.3.

Based on the obtained electrical characteristics, the threshold power value for one switching was calculated $P_{\text{th}} = U_{\text{th}} \cdot I_{\text{off}}$. For polycrystalline films, this value is 1.3 ± 0.1 MW, while for an array of nanocrystals it is ~ 20 times less and amounts to 54 ± 5 MW. This decrease in threshold power in the nanocrystal array is mainly attributable to lower threshold currents I_{off}, as well as lower heat dissipation during switching.

The magnitude of the current surge, as well as the threshold voltage, are largely determined by the geometry of the sample and contacts. It is known that a narrow channel with metallic conductivity (a conductive filament) is formed in VO_2 in the case of an electrically initiated phase transition [21–23]. At the same time, part of VO_2 remains in the semiconductor high-resistance state. Thus, the structure after an electrically initiated phase transition can be considered using a model of two parallel resistances, one of which corresponds to a thin channel with high conductivity (metallic state), and the second corresponds to a remaining part of VO_2 with low conductivity (semiconductor state). The value of the current surge during a phase transition in

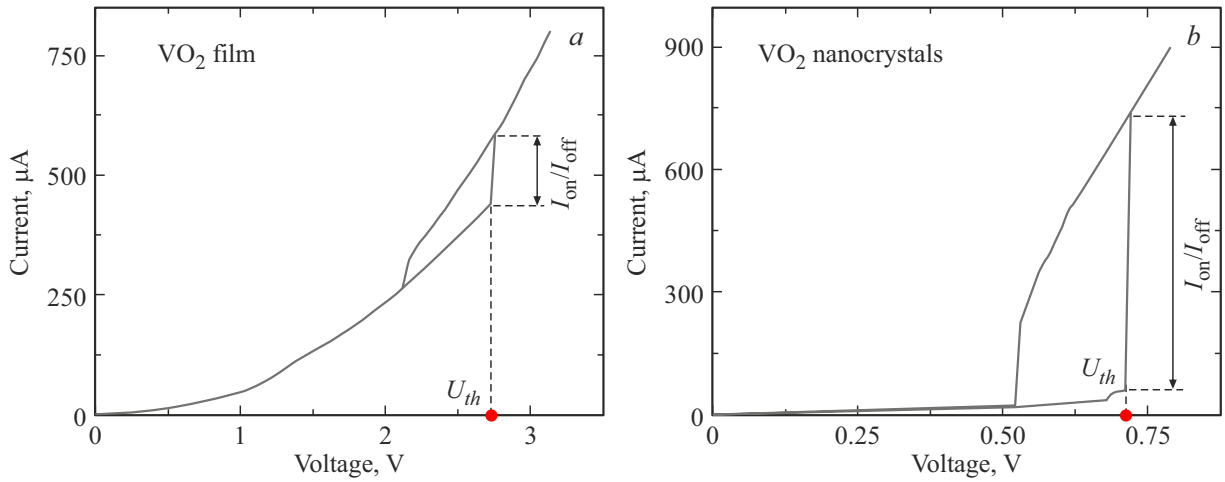

Figure 1. Electrical characteristics in the voltage source mode for a solid polycrystalline film of VO_2 (a) and an array of nanocrystals of VO_2 with a percentage of crystals filling the substrate surface $\sim 40\,\%$ (b).

such a model is determined by the equation

$$\frac{I_{\text{on}}}{I_{\text{off}}} = 1 + \left(\frac{S_{\text{met}}}{S_0}\right) \cdot \left(\frac{\rho_{\text{sem}}}{\rho_{\text{met}}} - 1\right), \qquad (1)$$

where I_{on} and I_{off} are the currents flowing in the metallic and semiconductor states, respectively; S_{met} is the area of the metal part of VO_2 after the transition; S_0 is the total area of VO_2 between two contacts; ρ_{sem} and ρ_{met} is the resistivity of semiconductor and metallic phases of VO_2 respectively.

It follows from the formula (1) that with a decrease in the percentage of crystals filling the substrate surface and, as a result, with a decrease in the total area of crystals between the two contacts S_0, the magnitude of the current surge will increase. This effect was observed experimentally when studying the electrical characteristics of samples with different percentages of crystals filling the substrate surface. For polycrystalline films of VO_2 with percentage of crystals covering the substrate surface, $95-100\,\%$, a current jump was observed during the phase transition by $1.5-3$ times (Figure 1, a). For an array of VO_2 nanocrystals with a percentage filling of the substrate surface with crystals $40-80\,\%$ current surge was $7-15$ times during the phase transition (Figure 1, b). A similar effect of an increase in the current surge with a decrease in the region of VO_2 between the contacts was observed for polycrystalline films in Ref. [24].

Studies of the electrical characteristics of single nanocrystals of VO_2 with a conductive AFM probe were carried out on individual crystals with a height of ~ 150 nm from the formed array. Figure 2, a shows the current-voltage curve of a single crystal VO_2 in the temperature range from 20 to 70 °C. When the voltage threshold is exceeded, sudden current surges associated with the phase transition are clearly visible. The threshold voltage decreases with increasing external temperature, and the current-voltage curve becomes linear at $T \geq 65 \pm 2\,^{\circ}\text{C}$, which corresponds to the metallic state of VO_2.

Figure 2, b shows the dependence of the threshold power per switching, expressed as $P_{\text{th}}(T) = U_{\text{th}}(T) \cdot I_{\text{off}}(T)$, on temperature. The behavior of this dependence can be explained within the framework of the heat balance equation $dQ/dt = P(t) - k\nabla T$, which determines the ratio between the Joule power $P(t)$ of the flowing current and the total power dissipated into the environment $k\nabla T$. The threshold power during electrical switching depends linearly on the outside temperature in the stationary state ($dQ/dt = 0$): $P_{\text{th}} = -\alpha(T_c - T_0)$, where T_0 is the outside temperature, T_c is the temperature of the phase transition in VO_2 [25,26]. The approximation of the experimental points $P_{\text{th}}(t)$ by a linear function allows us to estimate the temperature phase transition point, which corresponds to the intersection point with the abscissa axis and is $69 \pm 2\,^{\circ}\text{C}$. This value coincides with good accuracy with the temperature of the thermal phase transition 65 °C obtained by electrical measurements and with the value of the threshold temperature obtained by measuring the dependence of resistance on heating temperature of VO_2.

The value of the calculated slope coefficient α of the dependence $P_{\text{th}}(T_0)$ for a single nanocrystal of VO_2 is $(1.4 \pm 0.1) \cdot 10^{-9}$ W/K, which is $\sim 4-5$ orders of magnitude less than the previously obtained value $(7 \pm 0.8) \cdot 10^{-4}$ W/K for polycrystalline films [27]. This coefficient shows the total contribution of heat removal. The lower the coefficient α, the less heat is removed from the object under study to the external environment. A decrease in heat dissipation leads to a decrease in the switching threshold power. The calculated threshold power value for one resistive switching P_{th} at room temperature for a single nanocrystal of VO_2 with a height of ~ 150 nm is 40 ± 5 NW, which is almost by 4, orders of magnitude less than the obtained value for films and 3 orders of magnitude less than the value for arrays of nanocrystals of VO_2. Thus, an increase in the energy efficiency of a resistive switch based on a single nanocrystal of VO_2 by almost $3-5$ orders of magnitude, compared with a switch based on a solid film and based on an array of nanocrystals, occurs by reducing heat dissipation generated by a joule

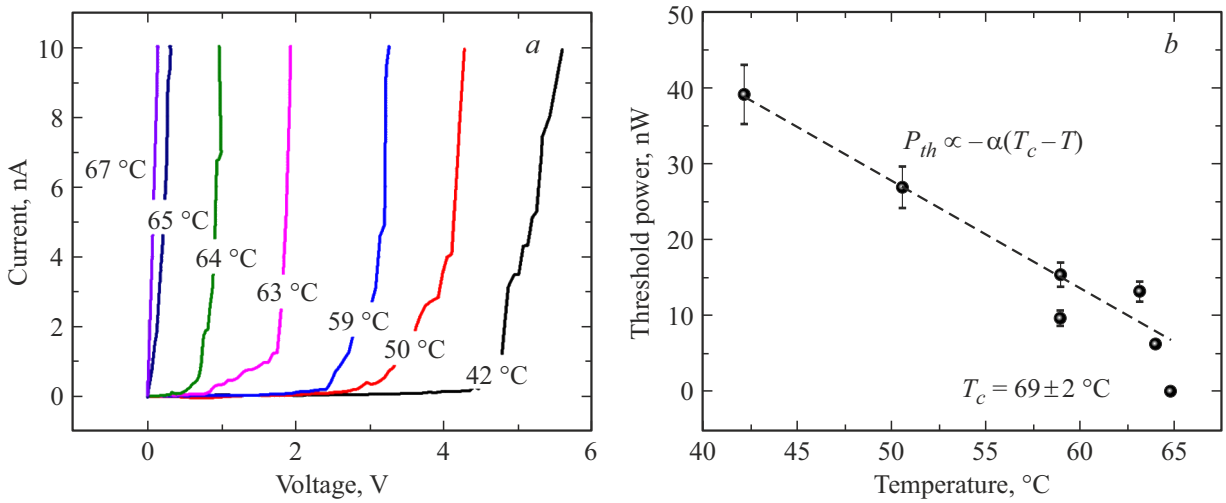

Figure 2. *a* — current-voltage curve of a single nanocrystal of VO_2 at various temperatures. *b* is a dependence of the switching threshold power on the temperature of a single nanocrystal of VO_2.

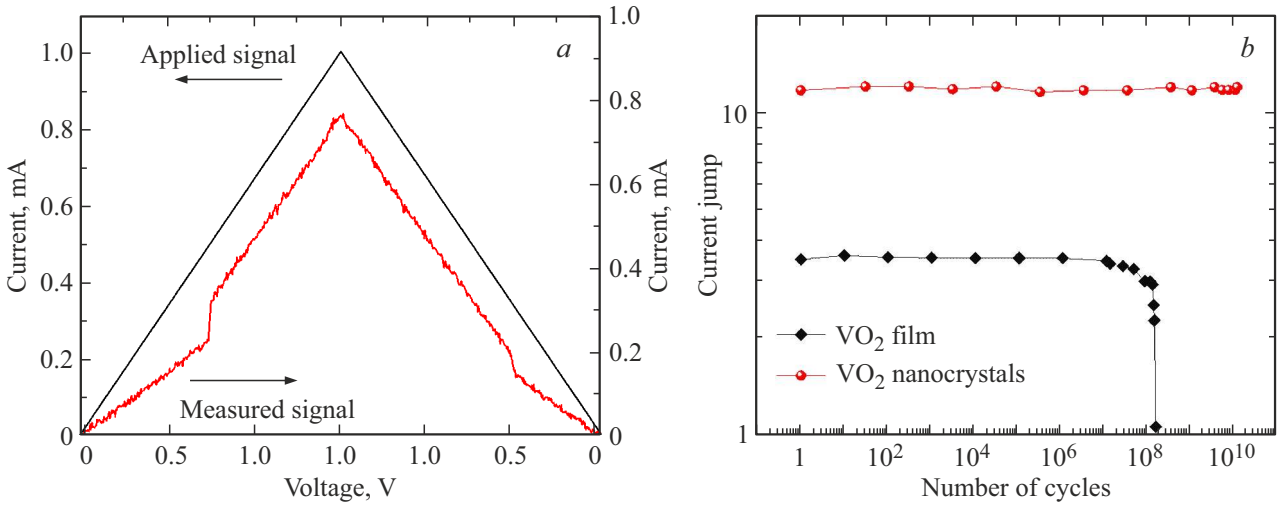

Figure 3. *a* — electrical characteristic for VO_2 structures with a current surge during an electrically initiated phase transition. *b* — change in the magnitude of the current surge during testing of films (black dots) and nanocrystals of VO_2 (red dots) for stability up to 10^{10} switching cycles.

by heating. The behavior of electrical characteristics under a triangular signal was studied to test the formed polycrystalline films and arrays of VO_2 nanocrystals for stability during multiple resistive switching (Figure 3, *a*). In this case, the current flowing through VO_2 was measured. Similar to the electrical characteristics obtained by direct current measurement, up to the threshold junction voltage U_{th}, VO_2 is in a semiconductor state with high resistance, and the measured signal is a linear dependence of current on voltage. There is a sharp jump in the current flowing through the sample at a voltage value of U_{th}, associated with the phase transition of VO_2 to the metallic state, which persists with a further increase in the amplitude of the applied voltage. When the amplitude of the applied voltage decreases from the maximum value to zero, VO_2 remains in the metallic state until a certain value is reached, at which a sharp drop in current occurs, associated with the phase transition of VO_2 back to the semiconductor state. It should be noted that the magnitude of the current surge during the transition from a metallic state to a semiconductor state is less than the magnitude of the current surge during the semiconductor-metal transition. This is due to the continuous decrease in the size of the conductive channel as the applied voltage decreases, which directly affects the magnitude of the current surge. During the reverse transition metal–semiconductor, the dimensions of the conducting channel are smaller than the similar dimensions of the formed channel during the forward transition, which leads to a smaller current surge.

We performed 10^{10} cycles of resistive switching. Figure 3, *b* shows the value of the current surge as a function of the number of switches performed. In samples with polycrystalline films of VO_2, the value of the current surge decreases sharply from ≈ 3 to 1 when the number of

switchings reaches $\approx 10^8$ (Figure 3, *b*, black points). Such a sharp decrease in the magnitude of the current surge indicates degradation of the film of VO_2 associated with accumulated mechanical stresses. For an array of VO_2 nanocrystals, the value of the current surge changed by less than 2% after 10^{10} switching cycles (Figure 3, *b*, red dots). At the same time, such a change by 2% may be due to the stability of the clamping contact, rather than to the degradation of the VO_2 crystal. This result indicates the high stability of the formed VO_2 nanocrystals and allows considering them as promising structures for durable and energy-efficient resistive switches.

4. Conclusion

In this work, polycrystalline films and arrays of VO_2 nanocrystals were formed, and resistive switching in them in the vertical geometry of contacts was investigated. Polycrystalline films were formed by chemical deposition from the gas phase, arrays of single nanocrystals were obtained from amorphous films synthesized by atomic layer deposition followed by annealing. X-ray phase analysis of the obtained structures showed the predominance of VO_2M1-phases. All structures exhibit a sharp jump in resistance up to 10^3 times just at a temperature of $\sim 68\,^\circ$C. It is shown that the threshold power per resistive switching decreases by 4–5 orders of magnitude during the transition from a solid film to a single nanocrystal and reaches a value of 40 ± 5 nW. It has been established that such a decrease in power consumption is associated with a decrease in heat dissipation from the nanocrystal compared to a solid film. The formed single nanocrystals of VO_2 have high stability under multiple resistive switching and are able to withstand at least 10^{10} cycles without significant changes in their properties. The use of single nanocrystals of VO_2 to create energy-efficient and stable resistive switches opens up new possibilities for their application in modern electronic devices.

Appendix

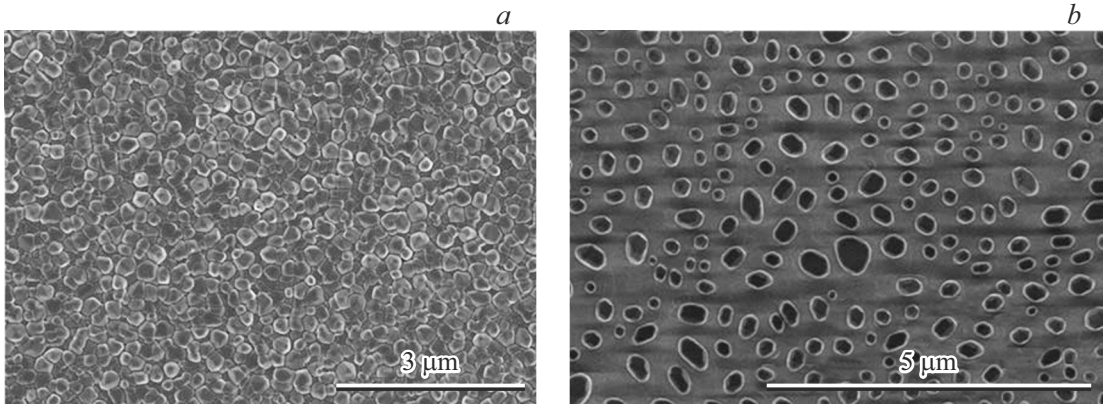

Figure. A.1. Characteristic SEM images for a synthesized polycrystalline film of VO_2 (*a*) formed by an array of VO_2 nanocrystals (*b*).

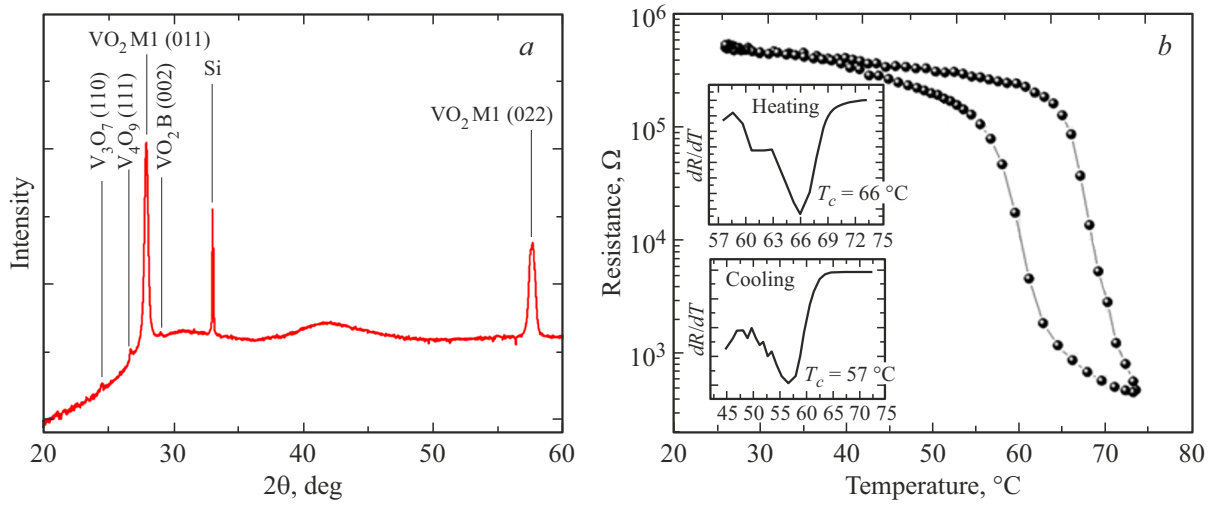

Figure A.2. *a* — diffractogram for an array of nanocrystals obtained at an annealing temperature 650 °C for 2 h. *b* — characteristic dependence of resistance on temperature for an array of nanocrystals. The insert shows the temperature of the phase transition in the forward and reverse branches as the logarithm of the derivative of the resistance with respect to temperature.

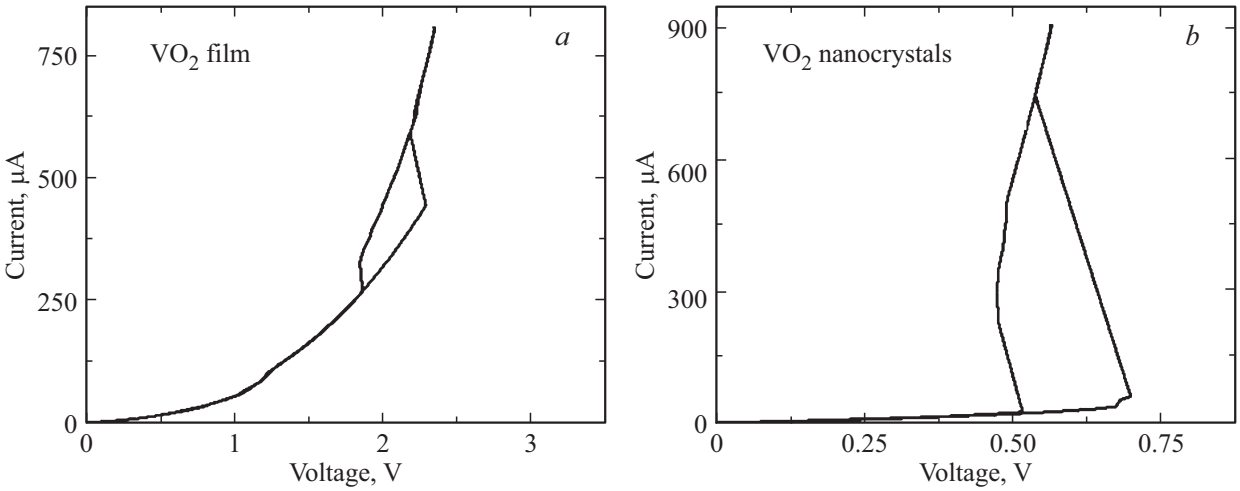

Figure A.3. Electrical characteristics in the current source mode for a solid polycrystalline film of VO_2 (a) and an array of nanocrystals of VO_2 with a percentage of filling crystals of the substrate surface $\sim 40\,\%$ (b).

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Conflict of interest

The authors declare that they have no conflict of interest.

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