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Synthesis and Resistive Switching of Nanocrystalline Vanadium Oxide Films †

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Abstract: The work is devoted to the study of the modes of synthesis of films of nanocrystalline vanadium oxide for the manufacture of resistive memory elements (ReRAM) of neuromorphic systems. The regularities of the influence of pulsed laser deposition modes on the morphology and electrophysical properties of vanadium oxide films were experimentally established considering the technological parameters of the substrate temperature and temperature of postgrowth annealing. Fabrication modes of nanocrystalline vanadium oxide films were determined with the high-resistance state $R_{HRS} = (123.42 \pm 21.77) \times 10^3\ \Omega$, the low-resistance state $R_{LRS} = (5.12 \pm 1.36) \times 10^2\ \Omega$, and the ratio $R_{HRS}/R_{LRS} = 253$, for the creation of elements of resistive memory with low power consumption and wide range of accepted possible resistance values. The results obtained can be used in the development of technological processes for the formation of nanocrystalline films of vanadium oxides for resistive memory elements in neuromorphic systems.

Keywords: nanotechnology; neuromorphic systems; memristor; ReRAM; resistive switching; nanocrystalline vanadium oxide; pulsed laser deposition

1. Introduction

Today, electronic computing systems are faced with several limitations that do not allow them to continue their rapid growth in speed and energy efficiency. Much of this is due to the «bottleneck problem» in the architecture on which most electronic computing is based - the von Neumann architecture [1,2]. One of the ways to solve this problem is the transition of computing systems from the von Neumann architecture to an architecture close to the structure of the human brain (neuromorphic systems) [3–5]. One of the methods for the technical implementation of a neuromorphic system is to fabricate memristor structures based on cross-bar technology, which makes it possible to create ultracompact 3d microcircuits with good scalability [6,7]. There are several promising memristor technologies on the electronics market (FeRAM, MRAM, PRAM, and ReRAM) [8,9]. ReRAM is nonvolatile, has low power consumption and multibitness, so is preferable for neuromorphic system creation. The principle of operation of ReRAM is based on the effect of resistive switching,—a change in the resistance of an oxide film between resistances in a high-resistance state (HRS) and a low-resistance state (LRS) as a result of the redistribution of oxygen vacancies in its volume under the action of an applied external electric field [10]. There are many materials that exhibit resistive switching effect, among which metal oxides (TiO_2, ZnO, ZrO_2, VO_2) stand out [11,12]. Recently, vanadium oxide has proven itself especially well for creating neuromoric systems. However, to create artificial intelligence systems based on vanadium oxide ReRAM elements, many experimental studies have yet to be carried out, in particular, studies of the influence of the electrophysical and morphological parameters of vanadium oxide films on the effect of resistive switching in them, which is the aim of this work.

2. Materials and Methods

Nanocrystalline vanadium oxide films were prepared using the Pioneer 180 pulsed laser deposition (PLD) system (Neocera Co., Beltsville, MD, USA), which makes it possible to control many technological parameters within a wide range. Si/TiN structures as a wafer were used. Nanocrystalline vanadium oxide films depositions were carried out considering the main control parameters of the PLD process: substrate temperature (25–650 °C), temperature (300–500 °C) of postgrowth annealing. To provide electrical contact to the bottom TiN electrode, nanocrystalline vanadium oxide films were deposited through a special shadow mask.

To study the electrophysical parameters of nanocrystalline vanadium oxide films, Hall measurement system Ecopia HMS-3000 (Ecopia Co., Korea) was used. The morphological parameters of the fabricated nanocrystalline vanadium oxide films are investigated using an Ntegra probe nanolaboratory (NT-MDT, Moscow, Russia) in semicontact mode. Experimental studies of the resistive switching in nanocrystalline vanadium oxide films were carried out using a Keithley 4200-SCS semiconductor measuring system (Keithley Instruments, Cleveland, Ohio, USA) and an EM-6070A submicron sensing device (Russia) with W probes. During the resistive switching investigation, TiN was grounded. At a point on the surface of the nanocrystalline vanadium oxide film, 50 current-voltage curves (CVC) were obtained from –1.6 to +1.6 V amplitude voltage sweep. Based on the obtained CVC, the dependence of the R_{HRS} and R_{LRS} on cycle number was built at the read voltage 0.5 V.

3. Results and Discussion

Figure 1 shows the experimental investigations of oxide vanadium film morphology grown at substrate temperature 650 °C. It was shown that the oxide vanadium film had a granular morphology (Figure 1c) with 232.6 ± 76.1 nm grain diameter (Figure 1c).

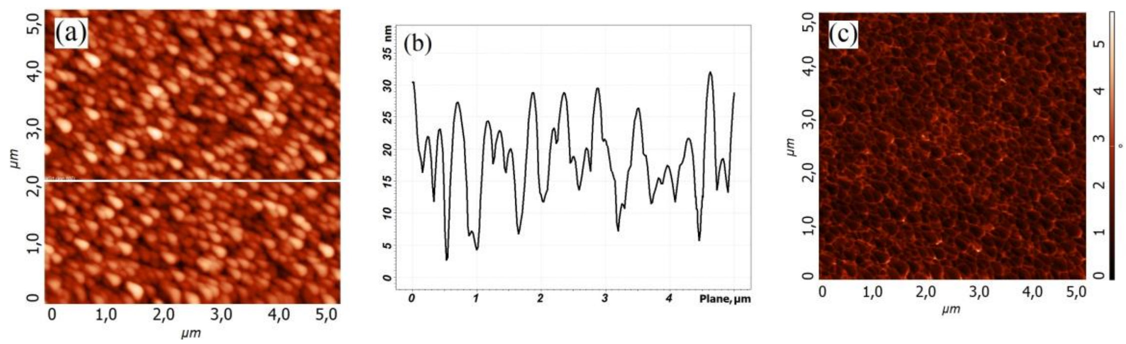

Figure 1. Nanocrystalline vanadium oxide film: (**a**)—AFM image; (**b**)—AFM cross-section; (**c**)—phase.

Analysis of the obtained experimental results showed that an increase in the substrate temperature (t_s) from 25 to 650 °C leads to an increase in the surface roughness from 4.3 ± 1.4 nm to 25.2 ± 4.4 nm (Figure 2a). The nonlinear dependence can be associated with the difference in the phase and stoichiometric composition of the nanocrystalline vanadium oxide films at different substrate temperatures. Furthermore, analysis of the obtained experimental results showed, that an increase in the annealing temperature (t_a) from 300 to 500 °C and leads to an increase in the resistivity of vanadium oxide films from $(2.03 \pm 0.05) \times 10^{-2}$ up to $(0.20 \pm 0.11) \times 10^{2}$ Ω·cm (Figure 2b). The a sharp increase in the resistivity at t_a above 400 °C can be explained by the presence of a V_2O_5 phase and an abrupt change in the phase and stoichiometric composition of the nanocrystalline vanadium oxide film as the annealing temperature approaches the V_2O_5 melting temperature (670 °C).

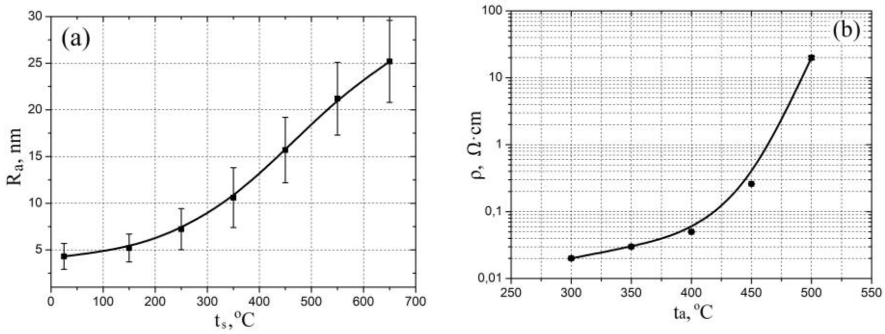

Figure 2. Dependence of the geometric and electrophysical parameters of a nanocrystalline vanadium oxide film on the control parameters of the PLD (**a**)—surface roughness on substrate temperature; (**b**)—resistivity on annealing temperature.

Analysis of the obtained experimental results of studying the effect of resistive switching showed that CVC has nonlinear bipolar behavior when presumably the electric potential gradient is the dominant parameter of the effect of resistive switching [13]. Resistive switching from HRS to LRS was observed at 1.37 ± 0.21 V (U_{SET}), and from LRS to HRS at −1.11±0.37 V (U_{RES}) (Figure 3a). In addition, analysis of experimental results for endurance test showed that R_{HRS} was $(123.42 \pm 21.77) \times 10^3$ Ω, R_{LRS} was $(5.12 \pm 1.36) \times 10^2$ Ω (Figure 3b). R_{HRS}/R_{LRS} ratio was about 253.

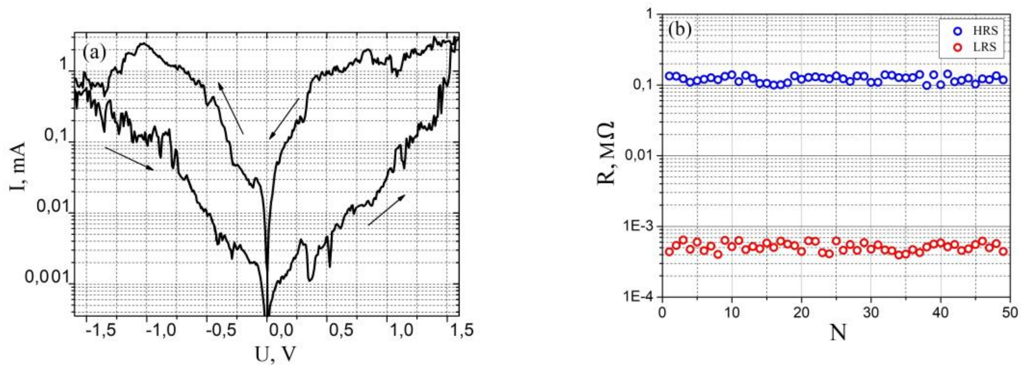

Figure 3. Investigation of resistive switching effect in nanocrystalline vanadium oxide film (**a**)—current-voltage characteristics; (**b**)—endurance test.

Dispersion of resistances R_{HRS} and R_{LRS} can be explained by the uneven redistribution of the oxygen vacancy concentration profile in the volume of the nanocrystalline film of vanadium oxide when resistive switching occurs.

4. Conclusions

In summary, we studied some of the modes of synthesis of films of nanocrystalline vanadium oxide for the manufacture of ReRAM elements for neuromorphic systems. The regularities of the influence of pulsed laser deposition modes on the morphology and electrophysical properties of vanadium oxide films were experimentally established considering the technological parameters of the substrate temperature, and the temperature of postgrowth annealing. It is shown that the change in substrate temperature from 25 to 650 °C, temperature of annealing in the range from 300 to 500 °C, makes it possible to obtain nanocrystalline films of vanadium oxide film surface roughness in the range from 4.3 ± 1.4 to 25.2 ± 5.4 nm, resistivity from (2.03 ± 0.05) × 10^{-2} up to (0.20 ± 0.11) × 10^2 Ω·cm. Resistive switching showed that U_{SET} = 1.37 ± 0.21 V, U_{RES} = −1.11 ± 0.37 V, R_{HRS} = (123.42 ± 21.77) × 10^3 Ω, R_{LRS} was (5.12 ± 1.36) × 10^2 Ω, and R_{HRS}/R_{LRS} ratio was about 253. The results obtained can be used in the development of technological processes for the formation of nanocrystalline films of vanadium oxides for resistive memory elements in neuromorphic systems.

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Conflicts of Interest: The authors declare no conflict of interest.

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