Laser formation of thin-film memristor structures based on vanadium dioxide

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Abstract. The thin films of VO₂ and the metal-oxide-metal (MOM)-structures of Au/VO₂/VO₂-x/Au based on them, which are promising for the use in neuromorphic electronic devices, have been obtained by the method of pulsed laser drop-free deposition on the c-sapphire substrates at room temperature. Using the cyclic I-V characteristics, a memristive effect has been revealed in the vertical geometry of the Au/VO₂/VO₂-x/Au MOM-structures. The x value was varied in the course of their growth by changing the pressure of buffer oxygen from 0.1 to 40 mTorr in the vacuum chamber, which provided the needed conductivity in the depleted injection layer. The dependence of memristive properties on the thickness of the semiconductor layer and concentration of the oxygen vacancies has been established. The oxygen pressure in the PLD method has been determined, at which the volatile behavior of the memristor resistive switching starts to appear at an oxide region thickness of 10/30 nm.

1. Introduction
The problems of processing large amounts of information require the development of bio-like ("neuromorphic") electronic devices or cognitive equipment [1]. The "neuromorphic" equipment of this kind with artificial intelligence capabilities can be based on the new types of devices, which present the artificial analogues of biological neural devices. The neuromorphic equipment is expected to reproduce the most characteristic electrical functions of the biological neural devices, to identify the features that may permit the computational functions of the brain to be reproduced. However, the implementation of even most elementary neural functions requires a large number of classical devices [2]. The neuromorphic functionality can be much easier implemented using the phenomenon of resistive switching in the circuits employing the memristors [3]. It has been found that the process of memristor switching between the states with different resistances is similar to formation and destruction of the bonds in the synapses of the brain [4]. In the memristors based on transition metal oxides, two main types of resistive switching, volatile and nonvolatile, can be implemented [5]. These two types of resistive switching allow realizing the principal hardware elements of neuromorphic systems that provide the basic functions of neurons and synapses [6]. Therefore, the memristor structures can be employed in modeling the work of the brain and creating artificial neural networks [7]. In the memristors, information is stored at the level of the electrophysical properties of the material, not the electric charge, which undoubtedly introduces an element of stability and helps to increase the density and speed of information recording, reading and erasing, as well as to reduce the power consumption. In addition, the memristor-based resistive memory offers small characteristic sizes of the memory element, non-volatility, and high durability [8]. Resistive switching of the memristors allows the
realization of basic neuronal and synaptic functions, and the necessary neuromorphic functions can be implemented through a combination of resistive switching devices and metal connections [9]. Thus, the memristors meet the requirements of modern non-volatile memory both to scaling and switching rate and are promising in creating the neuromorphic computer networks involving the new technology for data storage, processing and communication [10].

Volatile resistive switching is actually the case in the systems where a metal-insulator transition is observed. A drop in resistance occurs when a part of the material transforms from the insulating phase into the metal one under the action of an applied voltage. However, in a number of oxides (NbO2, VO2, and V2O3), the dominant metal-insulator transition mechanism still remains to be determined [11]. At present, the memristive effect shows up in many thin-film MOM structures based on the transition metals. The transition metal oxides are characterized by the presence of a large number of valence states, which allows different coordination of the metal with oxygen to be realized. This can result in a variety of crystal lattices and in changing of the state of electrons in the conduction band, which causes the unusual properties in electric transport [3]. With this in mind, it is necessary to improve the geometry, the material and the new ways of forming the active layer and memristor electrodes.

In this work we consider the thin VO2 films and the memristor structures based on them, obtained by pulsed laser deposition at room temperature of the substrate. The main characteristic that ensures the use of vanadium dioxide films is their displaying the effect of temperature-induced crystallographic transformation, accompanied by a change in the electrical and optical properties [12]. In addition to phase transition, the films of vanadium oxides possess the mechanism of electrical switching at room temperature by way of redistributing the ionized impurity of the positive mobile charges of oxygen vacancies (O2−), which provides a memristive effect [13]. The method of pulsed laser deposition in a drop-free mode makes possible producing the smooth, homogeneous high-quality films by eliminating the droplets flying from the target onto the substrate during the film growth [14]. The pulsed nature of the PLD method gives a high particle density in the plume and a high degree of ionization, which permits uniform spraying of the films with a thickness of several nanometers. The possibility of reducing the thickness of the layers of the MOM structure active region will enable the memristor properties to be studied over a wide range of thicknesses. The high energy of the particles in the laser plasma promotes reducing the crystallization temperature of the films up to room temperature. The deposition of films at room temperature of the substrate will provide the possibility of creating memristor structures on the flexible organic materials for which high-temperature processes are not applicable.

The aim of this work was to obtain the thin VO2 films by pulsed laser deposition in a drop-free mode at room temperature, to produce the MOM structures based on them, to study the structural and electrical properties of the produced films and the memristor properties of the resulting structures.

2. Experiment
The VO2 films and the Au/VO2/VO2-x/Au MOM structures based on them were produced by the method of pulsed laser deposition in a drop-free mode on the c-sapphire substrates using a mask technology. The value of x was varied during the growth of the MOM structures by changing the oxygen pressure in the vacuum chamber, which offered the required conductivity in the depleted VO2-x injection layer. The vanadium metal targets with a purity of 99.9% were ablated by radiation from an excimer KrF laser with the wavelength of 248 nm and the energy density on the target of at least 3 J/cm². The oxygen pressure in the vacuum chamber during the film growth was varied from 0.1 mTorr to 40 mTorr. The thicknesses of the obtained oxide layers ranged from 10 to 100 nm. The deposition of all the layers was carried out at room temperature of the substrate.

The crystal structure of the thin films of vanadium oxide was determined by x-ray diffraction. The studies were performed on a D8 Discover multipurpose X-ray diffractometer (Bruker-AXS, Germany) in the geometry 2θ–ω. The source of x-ray radiation was a 1.6 kW x-ray tube with a copper anode. A parallel beam with the divergence of 0.03° was formed by Goebel’s mirror. The X-ray beam width was 0.2 mm. The reflected beam intensity was measured using a LynxEye position-sensitive detector (angular resolution 0.015°).
The cyclic I–V characteristics of the memristor structures were measured with the aid of the probes by a double-contact circuit using a Keithley 2612. The probes were the thin tungsten needles coated with gold. A series of voltage pulses was applied to the test sample. The amplitude, duration, and duty cycle of the voltage pulses were set by the software. The envelope of the pulse train had a sawtooth shape symmetrical with respect to zero. The magnitude of the current for each voltage pulse was determined at the end of the pulse. The arrays of currents and voltages of one period of the envelope function were employed in constructing the graphs of a closed loop of the memristor structure I–V characteristic.

3. Results and discussion

The VO₂ films have been obtained on the c-sapphire substrates at various oxygen pressures in the vacuum chamber. The results of the x-ray investigation of the vanadium oxide films are presented in figure 1.

![Figure 1. The diffraction patterns of the VO₂ films with a thickness of 20 nm, obtained at an oxygen pressure of 2 mTorr (1) and 20 mTorr (2) in the deposition chamber.](image)

The figure shows that the films under study are amorphous. Both the diffraction patterns reveal only the (006) peak from the substrate of single-crystal c-sapphire. The results obtained indicate that the films deposited at room temperature of the substrate are amorphous regardless of the oxygen pressure during the growth.

A schematic representation of the memristor Au/VO₂/VO₂-x/Au MOM-structure produced by pulsed laser deposition on a c-sapphire substrate is shown in Fig. 2.

![Figure 2. A schematic representation of the memristor Au/VO₂/VO₂-x/Au MOM-structure obtained by pulsed laser deposition on a c-sapphire substrate.](image)

As can be seen from figure 2, a film of gold was grown on the surface of a single-crystal c-sapphire substrate in high vacuum, which served as the lower electrode. Then, a part of the lower electrode was coated with the thin films of depleted vanadium oxide VO₂-x and of a layer of vanadium dioxide VO₂. The targets in use were made from metallic vanadium. The contact pads of gold serving as the upper electrode were deposited on the surface of the VO₂ film through a mask having the form of a grid with oval holes of 0.36 mm² in area. Thus, a set of a large number of identical memristor structures located
on the same substrate was formed. One of the two measuring probes, being grounded, was placed on a free section of the lower electrode. The second probe was placed on the upper electrode of the memristor under study.

The resulting structures revealed a memristive effect. The cyclic CVC of the memristor structure is shown in figure 3.

As can be seen from figure 3, the I–V characteristic has the form of a hysteresis loop. This kind of dependence can be explained within the framework of the memristor model proposed in [13], and is based on the redistribution of the thickness of the active layers VO$_{2-x}$ and VO$_2$ of the memristor. According to this model, when the electric field displacement is applied to the control electrode, the diffusion of charged oxygen vacancies begins, which leads to a change in the effective thickness of each of the layers. The oxygen vacancies act in VO$_{2-x}$ as an n-type dopant, so the VO$_{2-x}$ layer has a significantly lower resistance than the defect-free VO$_2$ one.

The memristive properties of the Au/VO$_2$/VO$_{2-x}$/Au structure in which the thickness of the VO$_2$/VO$_{2-x}$ layers made 10/30 nm, were investigated at room temperature. The I-V characteristic of the structure is presented in figure 4.

The initial resistance of the memristor was 712 Ohms. In the course of voltage rise to 1.5 V in the mode of exponential dependence of current, the resistance falls to 60 Ohms. At the same time the dependence of current on voltage goes over to the linear ohmic mode which persists up to the voltage of 12 V. Here the structure changes its state, at 14 V the resistance falls to 48 Ohms and the I-V characteristic enters the ohmic mode. This value of resistance is retained to the limiting applied voltage of 15 V. On the inverse site of the positive branch at voltage reduction the resistance of the structure changes from the value
of 50 Ohms through a superficial minimum of 40 Ohms at -6V to the value of 45 Ohms at zero voltage at the end of the cycle.

In the laser synthesis of memristor structures from a vanadium metal target, an important role is played by the oxygen pressure in the vacuum chamber, which is the only source of vanadium oxidation during the formation of an oxide film. We have studied the dependence of the memristive properties on the concentration of oxygen vacancies in the depleted layer of the memristor structures at the 10/30 nm thickness of the oxide region VO2/VO2-x (figure 5).

Figure 5. The I–V characteristic of the memristor structure Au/VO2/VO2-x/Au in which the thickness of the VO2/VO2-x layers was 10/30 nm produced at an oxygen pressure of 0.1 mTorr (a) and 40 mTorr (b) in the vacuum chamber.

With an increase in the oxygen pressure up to 40 mTorr, the hysteresis loop clearly demonstrates resistive switching (figure 5a). At a low oxygen pressure of the order of 0.1 mTorr, the current-voltage characteristic demonstrates the volatile behavior of resistive switching of the memristor (figure 5b).

4. Conclusion
The thin VO2 films and the Au/VO2/VO2-x/Au MOM-structures based on them have been produced by the method of pulsed laser deposition in a drop-free mode on the c-sapphire substrates at room temperature. The MOM-structures containing VO2-x layers can undergo various types of insulator-metal transitions (IMT) in response to external disturbances, including an electric field or current. We have demonstrated the memristive effect in the MOM-structures of Au/VO2/VO2-x/Au in the vertical geometry with different contents of oxygen vacancies and thicknesses of the oxide region. The structures were grown by the drop-free method of pulsed laser deposition from the metal targets using a mask technology and studied at room temperature. The behavior of the I–V characteristics of the memristive structures during cyclic scanning of the applied voltage has been investigated. The dependence of the memristive properties on the thickness of the semiconductor layer and the concentration of oxygen vacancies has been obtained. The oxygen pressure in the PLD method has been determined, at which the volatile behavior of the memristor resistive switching starts to appear at an oxide region thickness of 10/30 nm. Thus, the memristor based on Au/VO2/VO2-x/Au in the vertical geometry is promising for the use in the neuromorphic electronic devices as a neuristor with volatile resistive switching.

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