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Optimization of switching memristor structures based on HfO_x using electron beam exposure

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The electrophysical properties of memristors based on HfO_x ($x \sim 1.8$) irradiated with an electron beam in an area comparable in size to the cross-section of the filament are investigated. These properties are compared with memristors of a similar structure made without the use of local electron beam influence on the hafnium oxide layer. It is shown that such an effect leads to a decrease in the amplitude and voltage variance of switching states of the memristor. Charge transport in both types of memristors has been studied, and the nature of the observed differences is discussed.

Keywords: hafnium oxide, memristor, electron beam, scanning electron microscope, space-charge limited current.

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1. Introduction

Memristor structures (ReRAM), whose principle of operation is based on resistive switching of the dielectric layer between metal electrodes under the action of a sufficient electric field, are promising to be used as electronic memory cells. The change of state when an electric field is applied to the dielectric is due to the electrodiffusion of atoms of the metal electrode into the dielectric layer [1] or oxygen vacancies present in them [2]. This results in the formation or destruction of a stable conducting channel between the electrodes — the filament. Resistance switching in memristors can be either two-level or multilevel — with intermediate states between low resistance state (LRS) and high resistance state (HRS) [3]. One of the unresolved problems of memristor structures is the need for their forming, which is the process of the conductive filament nucleation when an electric field of sufficient magnitude is applied to the structure for the first time. Typically, the forming voltage is much higher than the switching voltage of the memristor [4]. Another challenge is the change in state switching voltage during the cyclic rewriting of information into the memory cell. This is probably due to the randomness of the filament formation and fracture process, as well as the formation of competing filaments [5].

The authors have previously shown that the local electron beam irradiation of the oxide layer of the TaN/HfO_x/Ni memristor leads to a decrease in the values of resistive switching voltages, as well as the variation of resistances in the LRS and HRS states in comparison with a memristor of a similar structure without such an impact [6]. It was found that the formation of crystalline phases occurs in the exposed region. However, the memristors obtained in this way required the forming process. It appears that local electron-beam exposure leads to the formation of a conductive filament nucleation center, which may be similar to the partially dissolved filament in the high-resistance state of the memristor without irradiation. The purpose of this paper is to continue comparing the electrophysical parameters of TaN/HfO_x/Ni structures before and after irradiation, to verify the reproducibility of previously obtained results, and to compare the charge transfer mechanisms in the initial state of the memristor with irradiation and the high-resistance state of the memristor without irradiation.

2. Experiment procedure

In this paper, TaN/HfO_x/Ni structures are studied. The TaN layer was deposited on Si/SiO_2 substrate by ion beam sputtering deposition method. The HfO_x layer was deposited by the same method at an oxygen partial pressure of $2.2 \cdot 10^{-3}$ Pa, which corresponds to $x \sim 1.8$ [7]. The thickness of the bottom electrode was 50 nm, and that of the dielectric was 30 nm. After that, some of the samples were exposed to the electron beam irradiation in a Hitachi SU8220 scanning electron microscope (SEM) chamber in the $50 \times 38\,nm^2$ region by an electron beam with a diameter of 1.5 nm, an electron energy of 15 keV, and an electron emission current of 1 nA. The exposure was performed for 15 min, which corresponds to the electron fluence $\Phi = 3.0 \cdot 10^{23}\,cm^{-2}$, whereby the effect of local electron-beam crystallisation and reduction of the variation of electrophysical parameters of the memristor was previously observed. The other part of the samples was not exposed to electron irradiation. After that, a layer of top Ni electrodes of square shape with a side of 200 μm was deposited on all samples. The contacts were deposited by electron-beam evaporation through a mask. A special holder was used for the samples exposed to electron-beam influence to ensure the alignment of the irradiated areas with the top electrodes.

The resistive switching of the structures was studied using an Agilent B1500A semiconductor analyser. The current-voltage curve in $T = 200-350\,\mathrm{K}$ temperature range was measured using a Linkam LTS420E PB4 temperature stage on a Keithley 2400 source-meter. The voltage was varied in steps of 0.05 V at a rate of 0.25 V/s to avoid significant heating of the structure and deviation from the target temperature. The bias current had minimal influence on the obtained current-voltage curve due to the small capacitance of the structure and sufficient duration of the voltage sweep.

3. Results and discussion

Memristors on samples of both types exhibited a resistive switching effect of the bipolar type (Figure 1). Both the unirradiated and irradiated samples required forming, during which a current compliance of $I_{cc} = 1.0\,\mathrm{mA}$ was set to avoid damage to the structures. In both cases, the forming voltage was close to the subsequent resistive switching voltages. The switching voltages from the low-resistance state to the high-resistance state and back (U_{set} and U_{reset} respectively) were about $\pm 3.5-4.5\,\mathrm{V}$ for the memristors on the sample without irradiation and about $\pm 1.3-1.5\,\mathrm{V}$ for the memristors on the sample with irradiation. We have previously observed a similar decrease in switching voltages to these values for hafnium oxide-based memristors with a lower degree of oxygen depletion $x \sim 1.81$, when the composition was near the upper limit of the range at which resistive switching is observed, irradiated at the same value of $\Phi = 3.0 \cdot 10^{23}\,\mathrm{cm}^{-2}$ [6].

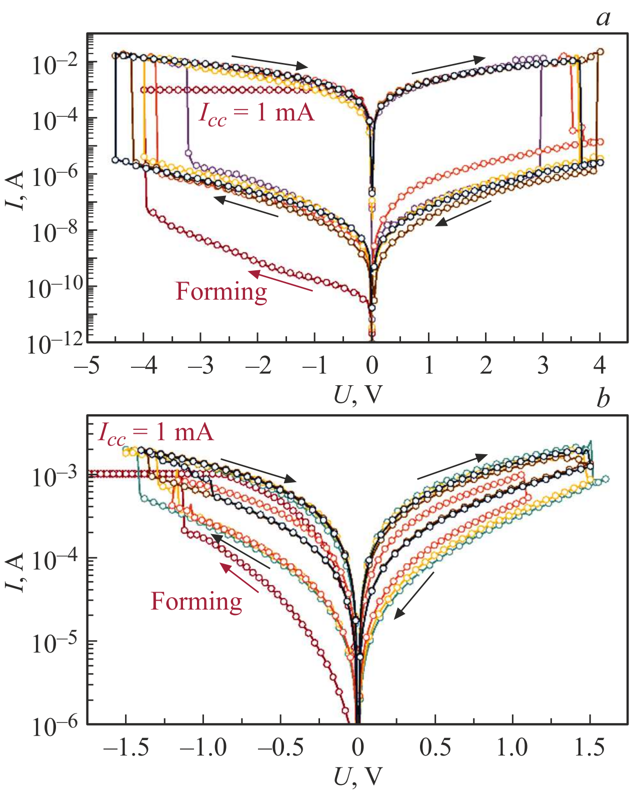

Figure 1. The forming and resistive switching current-voltage curves of TaN/HfO$_x$/Ni memristor structures with $x \sim 1.8$ at $T = 300\,\mathrm{K}$: *a* — unirradiated structure; *b* — memristor whose layer was exposed to electron-beam irradiation with $\Phi = 3.0 \cdot 10^{23}\,\mathrm{cm}^{-2}$. (A color version of the figure is provided in the online version of the paper).

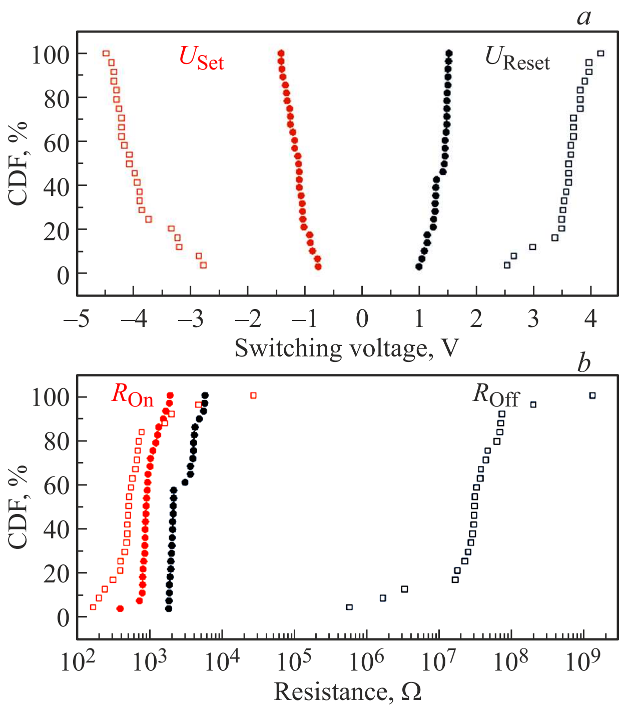

Figure 2. Cumulative distribution functions: *a* — resistive switching voltages; *b* — resistances. The data are for LRS and HRS TaN/HfO$_x$/Ni with $x \sim 1.8$, memristors whose oxide layer was electron-beam exposed with $\Phi = 3.0 \cdot 10^{23}\,\mathrm{cm}^{-2}$ (round symbols) and without such exposure (square symbols). (A color version of the figure is provided in the online version of the paper.)

Figure 2 shows the cumulative distribution functions of resistive switching voltages (U_{set} and U_{reset}, Figure 2, *a*) and resistances in LRS and HRS (R_{on} and R_{off} respectively, Figure 2, *b*) for TaN/HfO$_x$/Ni memristors with $x \sim 1.8$ under fluence irradiation $\Phi = 3.0 \cdot 10^{23}\,\mathrm{cm}^{-2}$ and without it. From the analysis of the data, it follows that local electron-beam exposure resulted in a decrease in the standard deviation of the U_{set} values from 0.49 to 0.19 V, U_{reset} — from 0.38 to 0.12 V. As with the previously studied sample with $x \sim 1.81$, irradiated at the same value of Φ, the ratio of $R_{\mathrm{Off}}/R_{\mathrm{On}}$ was small and was ~ 2. Compared to the unirradiated sample of the same composition, the coefficient of variation (the ratio of the standard deviation to the mean) decreased significantly: for R_{on} from 1.44 to 0.28, and for R_{off} from 2.82 to 0.42.

Unlike the resistive switching voltages and resistances in LRS and HRS, the large variation from memristor to memristor on the irradiated sample was demonstrated by the forming voltage (± 0.5 V) and the resistance in the initial state (several orders of magnitude). Similar situation is common for memristors that have not been exposed to electron-beam irradiation. Figure 3 shows the current-voltage curves for the high-resistance state of the memristor on the TaN/HfO$_x$/Ni with $x \sim 1.8$ sample without irradiation (Figure 3, *a*) and those for the pre-forming (initial) state of the memristor irradiated at $\Phi = 3.0 \cdot 10^{23}$ cm^{-2} (Figure 3, *b*). It can be seen that in the high-resistance state of the memristor without irradiation in this temperature range there is a rather strong temperature shift of the current-voltage curve by ~ 1.5 order. At the same time in the initial state of the irradiated memristor it is only of the order of ~ 0.5. Previously, the authors have shown that in the HRS state of memristors with TaN/HfO$_x$/Ni structure there is a nonmetallic filament, which differs from the filament in the LRS state by composition and smaller cross-sectional size [8]. Charge transport in this case for HRS was determined in the linear part of the current-voltage curve by the mechanism of thermal generation of charge carriers due to donor-like defects (1), and in the quadratic part — by the mechanism of trap-mediated space-charge-limited current (SCLC) (2):

$$j_{\text{Ohm}} = qn\mu_n \frac{U}{d}, \tag{1}$$

$$n = \frac{2N_d}{1 + \sqrt{1 + \frac{2N_d}{N_c} \exp\left(\frac{E_c - E_d}{kT}\right)}},$$

$$N_c = 2(2\pi m^* kT/h^3)^{3/2},$$

$$j_{\text{sclc}} = \frac{9}{8} \kappa \varepsilon_0 \mu_n \theta \frac{U^2}{d^3},$$

$$\theta = \frac{N_c}{N_t} \exp\left(-\frac{E_c - E_t}{kT}\right), \tag{2}$$

where q — electron charge, n — free electron concentration in the oxide, μ_n — electron mobility, d — dielectric thickness, N_c — effective density of electron states in the conduction band, m^* — effective electron mass, k — Boltzmann constant, h — Planck constant N_d — concentration of donor-like defects, $(E_c - E_d)$ — ionisation energy of donor-like defects, κ — dielectric permittivity of the oxide layer, ε_0 — electrical constant, θ — fraction of free electrons from all injected electrons (free and captured), N_t — concentration of traps for charge carriers, $(E_c - E_t)$ — depth of traps.

For HfO$_x$-based samples with a sufficiently strong degree of oxygen depletion at large voltage values, the contribution to the total current, in addition to the thin filament, is given by the dielectric bulk in which charge transport is determined by the trap-mediated mechanism with an exponential trap distribution (3):

$$j_{\text{sclc}} = \mu_n N_c q^{1-l} \left(\frac{\kappa\varepsilon_0}{N_0} \frac{l}{l+1}\right)^l \left(\frac{2l+1}{l+1}\right)^{l+1} \frac{U^{l+1}}{d^{2l+1}}, \tag{3}$$

where $l = T_t/T$, T_t — temperature parameter which characterizes the exponential trap distribution, $N_0 = N_t' k \cdot T_t$ — concentration of traps per energy unit at the boundary of the conduction zone, N_t' — total concentration of traps in the oxide volume.

The analysis of experimental current-voltage curves at different temperatures for the TaN/HfO$_x$/Ni memristor without irradiation in the HRS state and for a similar memristor with irradiation in the pre-forming state showed that in both cases they are well approximated by the calculated curves obtained from equations (1)–(3) (Figure 3). At the same time, the parameters of equation (3) describing the contribution to the conductivity of the bulk part of the dielectric layer of the memristor, in both cases are practically the same: $l = 3.0$, the value of N_t' in the first case was $9.0 \cdot 10^{20}$ cm^{-3}, and in the second — $7.0 \cdot 10^{20}$ cm^{-3}. The small difference is probably due to small random fluctuations in the growth parameters of the oxide layer of the samples. However, the current-voltage curves of the memristor obtained using local electron beam exposure in the pre-forming state cannot be

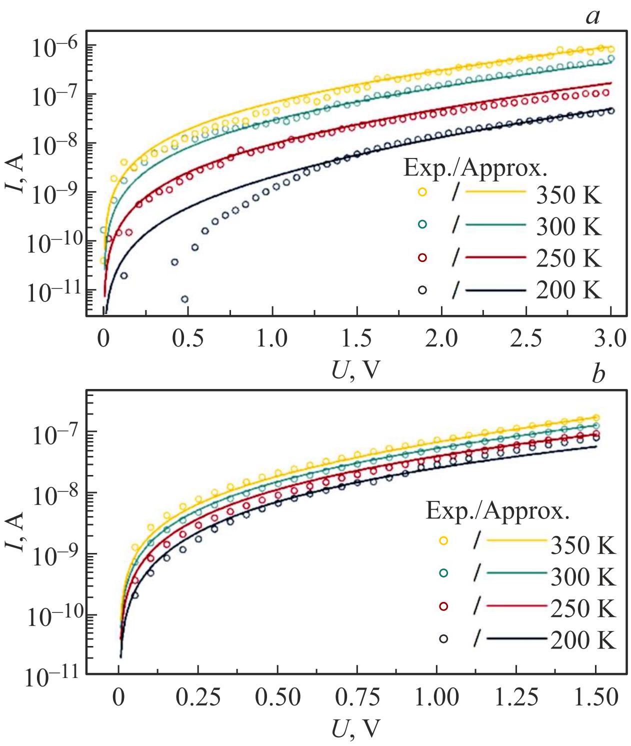

Figure 3. The current-voltage curve of TaN/HfO$_x$/Ni memristors with $x \sim 1.8$ in HRS state: *a* — without irradiation; *b* — memristor whose oxide layer was exposed to electron-beam irradiation with $\Phi = 3.0 \cdot 10^{23}$ cm^{-2} in the pre-forming state. Dots show experimental data, and lines denote calculated current-voltage curves. (A color version of the figure is provided in the online version of the paper.)

described by the contribution from the dielectric volume alone. Therefore, it was assumed that the conductive filament nucleation center also contributes to the charge transport, similar to the partially dissolved filament in the HRS state of the memristor without irradiation. The values of $m^* = 0.42m_0$ (where m_0 — electron mass), $\mu = 4\,\mathrm{cm}^2/(\mathrm{V}\cdot\mathrm{s})$ and $\kappa = 20$, were found to be common in both cases, which is consistent with the literature [9]. For the memristor without irradiation, the concentration and ionisation energy of donor-like defects in the filament were $5.0 \cdot 10^{17}\,\mathrm{cm}^{-3}$ and 300 meV, respectively, and traps — $6.0 \cdot 10^{18}\,\mathrm{cm}^{-3}$ and 110 meV, respectively. In turn, the N_d and $(E_c - E_d)$ values for the conductive filament nucleation center in the irradiated memristor were $1.0 \cdot 10^{18}\,\mathrm{cm}^{-3}$ and 100 meV, respectively, and the N_t and $(E_c - E_t)$ were $1.0 \cdot 10^{18}\,\mathrm{cm}^{-3}$ and 30 meV, respectively.

The ionisation energy of donor-like defects in the irradiated memristor in the pre-forming state with a value of ~ 100 meV is rather closer to the values we observed previously for non-irradiated memristors in the LRS [8] state. The trap ionisation energy for the irradiated memristor in the pre-forming state of about a few tens meV was much lower than the values observed earlier and in this paper for the HRS state of memristors without local electron-beam exposure, where it is about an order of magnitude higher. However, in both cases the charge transport is qualitatively described within the same charge transport mechanisms. Thus, apparently, the structure of the conductive filament nucleation center formed during the electron-beam irradiation is very close to the conducting filament in the high-resistance state of the memristor.

4. Conclusion

In this paper, two types of TaN/HfO_x/Ni with $x \sim 1.8$ structures were compared. The dielectric in one type of structures was exposed to the electron-beam irradiation with fluence $\Phi = 3.0 \cdot 10^{23}\,\mathrm{cm}^{-2}$. In the other type of structures the HfO_x was not exposed to irradiation. As a result of current-voltage curve measurements, it was discovered that the switching voltages between the states — U_{set} and U_{reset} were $\pm 3.5{-}4.5$ V for structures without irradiation and $\pm 1.3{-}1.5$ V for memristors with irradiated HfO_x. It is also shown that local electron irradiation of the HfO_x film resulted in a decrease in the standard deviation of the U_{set} from 0.49 to 0.19 V and U_{reset} from 0.38 to 0.12 V. It is observed that the ratio of resistances in the high and low impedance states $R_{\mathrm{off}}/R_{\mathrm{on}} \sim 2$ for the structure with irradiated HfO_x has a small value relative to the sample with unirradiated dielectric. The coefficient of variance decreased significantly after exposure of the dielectric to the electron beam: from 1.44 to 0.28 for R_{on} and from 2.82 to 0.42 for R_{off}, suggesting that the stability of the resistive switching of the memristor increased after irradiation. The analysis of experimental current-voltage curves at different temperatures shows that the conductive filament nucleation center in the HfO_x layer created during local electron-beam irradiation contributes to the conductivity of the memristor in the pre-forming state and is close to the filament in the high resistive state of the memristor without such irradiation in its properties.

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Conflict of interest

The authors declare that they have no conflict of interest.

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