Forming-free resistive switching in nanocrystalline hafnium oxide films

V A Smirnov, R V Tominov, V I Avilov, A A Avakyan and O A Ageev
Institute of Nanotechnologies, Electronics and Equipment Engineering, Southern Federal University, 347928 Taganrog, Russia

roman.tominov@gmail.com

Abstract. This work presents the results of the investigations of resistive switching effect in Si(100)/HfO$_2$ structure. It was shown that resistive switching from HRS to LRS occurred at 0.4±0.1 V, and from LRS to HRS at -0.5±0.1 V. An increase in the sweep voltage from 1 to 5 V led to a decrease in the HRS/LRS ratio from 606±36 to 204±1. Thus, it was shown that the nanocrystalline HfO$_2$ film resistance varied within two orders of magnitude at a sweep voltage of 1 V within 15 measurements. The results can be useful for manufacturing neuromorphic systems based on forming-free nanocrystalline HfO$_2$ films.

1. Introduction
Brain-based computing is a new area that can expand the rich of information technology beyond the von Neumann paradigm [1,2]. Every year, more and more popular solutions to the problems associated with processing heterogeneous «noisy» data appear: image recognition in real time, diagnostics of various processes, as well as in applications related to self-learning and adaptive control systems [3,4]. One of the ways to achieve this goal is the creation of integrated circuits (IC) based on memristors, which are key elements for simulating high-density biological neurons, interconnected using special channels – synapses. It should be noted that in the biological brain the number of synapses exceeds the number of neurons by 3-4 orders of magnitude, which implies that for the technical implementation of ICs based on memristor structures, memory elements must have small geometric dimensions to achieve a high degree of integration. An analysis of articles has shown that one of the most suitable elements for the technical implementation of memristors for neuromorphic structures is non-volatile resistive memory (ReRAM, which has a small cell size of several nanometres, a high integration density, a high speed and low power consumption, which allows simulating mass concurrency and low-power computing previously observed in the human brain [5-14]. The human brain has a high degree of connectivity, and any neuron can have up to 10,000 connections with other neurons. An array of ReRAM elements provides the ability to emulate such connectivity. The principle of operation of ReRAM is based on the effect of resistive switching – changing the resistance of a thin oxide film in the range of values between the resistance in the low-resistance state (LRS) and that in the high-resistance state (HRS), when an external electric field is applied. An analysis of the publications has shown that structures based on binary metal oxides are promising for creating neuromorphic systems; nanocrystalline hafnium oxide (HfO$_2$) can be particularly distinguished [5-18]. Nanocrystalline HfO$_2$ shows forming-free resistive switching with high speed, low energy consumption, high HRS/LRS ratio, and also a sufficiently large number of switching cycles. However, for the manufacture of neuromorphic structures based on hafnium oxide, there are currently no systematic modes of studying the effect of sweep voltage on the HRS/LRS ratio. There are many methods for manufacturing thin films of hafnium oxide; however, it was decided...
to use the pulsed laser deposition (PLD) method, which allows the formation of films in a wide range of electrophysical and morphological parameters with an acceptable growth rate. In the process of studying the effect of resistive switching, a need arises for a local study of the morphology of thin oxide films. Atomic force microscopy (AFM) is one of the promising methods that can effectively solve this problem [19-27]. Thus, the aim of this work is to study the effect of resistive switching in thin films of hafnium oxide, in particular, to study the effect of sweep voltage on the HRS/LRS ratio.

2. Experimental
To carry out experimental studies of the resistive switching in nanocrystalline HfO$_2$ film, the sample was prepared using pulsed laser deposition equipment Pioneer 180 (Neocera Inc., USA). Silicon substrate Si with a crystallographic orientation (100) and 10 Ω·cm resistivity was used as a wafer. Deposition was performed under the following conditions: wafer temperature 30°C, target-wafer distance 50 mm, O$_2$ pressure 1 mTorr, pulse energy 300 mJ, number of pulses 30000, and frequency 10 Hz. To provide electrical contact to the Si substrate, the HfO$_2$ film was deposited through a special mask pattern. As a result, HfO$_2$ did not precipitate on a template-protected area of the Si surface.

AFM-images of HfO$_2$ film surface were obtained and processed using atomic-force microscope Solver P47 Pro (NT-MDT, Russia) and Image Analysis 1.1, respectively. Electrical properties of obtained HfO$_2$ film were measured by Ecopia HMS-3000 equipment (Ecopia Co., Republic of Korea). Electric measurements were carried out using semiconductor characterization system Keithley 4200-SCS (Keithley, USA) with W probes. During experiment, TiN layer was grounded. To avoid electrical breakdown of the HfO$_2$ film, a current limit of 1 mA during electrical measurements was set. Current-voltage characteristics were measured at the same point (endurance test) and in different points (homogeneity test) at different voltage sweeps from 1 to 5 V. Based on the results obtained, the dependence of HRS/LRS ratio on sweep voltage was built. The curves were analysed using Origin 8.1 software.

3. Results and discussion
The results of experimental studies showed that nanocrystalline HfO$_2$ film surface had a granular structure with 0.25±0.08 µm grain size (Fig. 1a,c) and 12±3 nm roughness (Fig. 1b). Studies of electrophysical parameters showed that nanocrystalline HfO$_2$ film had $6.5\times10^{19}$ cm$^{-3}$ electron volume concentration, 12 cm$^2$/V·s electron mobility, and 4.2×10$^{-3}$ Ω·cm resistivity.

Figure 2a shows average current-voltage characteristics (CVC) of Si(100)/HfO$_2$ structure at –1 to +1 voltage sweep, performed from the 15 current-voltage curves at the same point. It was shown that Si(100)/HfO$_2$ structure exhibited a nonlinear bipolar behaviour, when the electric potential gradient was the dominant parameter of resistive switching effect [24]. Resistive switching from HRS to LRS occurred at 0.4±0.1 V (SET), and from LRS to HRS at -0.5±0.1 V (RESET) (Fig. 2a). Based on the

Figure 1. Investigation of the formed HfO$_2$ film: (a) AFM-image; (b) cross-section profile along white line on (a); (c) phase.
obtained CVC for different voltage sweeps, the dependence of the HRS/LRS ratio on the sweep voltage was built. Analysis of the results showed, that an increase in the sweep voltage from 1 to 5V led to a decrease in the HRS/LRS ratio from 606±36 to 204±11 (Fig. 2b). The obtained result can be explained by a decrease in the dissolution length of the oxygen vacancy nanofilaments with an increase in the sweep voltage, and, as a consequence, an increase in the current through the HfO$_2$ film.

Investigations of effect of resistive switching uniformity in Si(100)/HfO$_2$ structure in a single point (endurance test) and in different points on the film surface (homogeneity test) were performed at voltage sweep, at which the maximum HRS/LRS ratio was observed, i.e. at 1V. Reading voltage was 0.3 V. It was shown, that for endurance test HRS was 298±25 kΩ, LRS was 0.51±0.05 kΩ (Fig. 3a), and for homogeneity test HRS was 304±147 kΩ, LRS was 0.5±0.2 kΩ (Fig. 3b). It was shown, that resistance confidence interval of endurance and homogeneity tests varied 4.3 times for HRS and 3.5 times for LRS. It can be explained by the heterogeneity of the HfO$_2$ film surface morphology and also by the different concentration of oxygen vacancies in volume at different points on the HfO$_2$ film surface. Thus, it was shown that the nanocrystalline HfO$_2$ film resistance varied within two orders of magnitude at a sweep voltage of 1 V within 15 measurements.

4. Conclusion
In summary, we investigated effect of resistive switching in a nanocrystalline HfO$_2$ film formed by pulse laser deposition. The results of experimental studies, obtained using AFM, showed that nanocrystalline HfO$_2$ film had a granular structure with 0.25±0.08 µm grain size and nm with roughness 12±3 nm.
Electrophysical parameters of nanocrystalline HfO$_2$ film were investigated. It was shown, that volume concentration was $6.5 \times 10^{19}$ cm$^{-3}$, mobility was 12 cm$^2$/V·s, and resistivity was $4.2 \times 10^3$ Ω cm. Resistive switching from HRS to LRS occurred at 0.4±0.1 V, and from LRS to HRS at -0.51±0.11 V. The experimental dependence of HRS/LRS ratio on sweep voltage was built. It was shown, that an increase in the sweep voltage from 1 to 5V led to a decrease in the HRS/LRS ratio from 606±36 to 204±11. The results of experimental studies of resistances for sweep voltage 1V showed that for endurance test HRS and LRS were 298±25 kΩ and 0.51±0.05 kΩ, respectively, and for homogeneity test 304±147 kΩ and 0.5±0.2 kΩ, respectively. Thus, it was shown that the nanocrystalline HfO$_2$ film resistance varied within two orders of magnitude at a sweep voltage of 1 V within 15 measurements. The results can be useful for manufacturing neuromorphic systems based on forming-free nanocrystalline HfO$_2$ films.

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