Improving Characteristic Parameters of Memristor Based on HfO\textsubscript{2} Active Layer

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Abstract. The improvement of the characteristic parameters of the memristor depends on the factors such as thickness and surface area of the active layer. These parameters define leakage currents, which is the main disadvantage of the memory storage device and to improve the electrical features the leakage currents must be dropped to the zero in ideal case. In the presented work is described the electrical isolation of the active layer from the substrate by the thin layer of photoresist, which is an electrical insulator. For reducing area was used the new fotomask, which is able to reduce area 100 times. The memristor structures are designed in the form of "crossbars", which allows us to individually investigate each memristor and create a database with the possibility of incorporating it into the microchip in the future. In this work is presented also research outcomes regarding to selection memristor’s contacts and active layers. As contacts are overviewed tungsten (W), titanium nitride (TiN) and aluminum (Al). Is considered metal and transition metal oxides as active layers WO\textsubscript{x}, HfO\textsubscript{2}, WO\textsubscript{x} + HfO\textsubscript{2}, HfO\textsubscript{2} + HfO\textsubscript{x}. The oxide electrical and structural properties is defined from I-V, C-V, XRD and XPS characteristics.

1. Introduction
In modern technologies, and especially in micro and nanoelectronics, the dimensions of the components of the circuit and the problems of insulation between the elements play a crucial role. When forming different passive elements, important their structure and isolation each to other. In parallel to development of technologies, the degree of their integration scale increases, new electrical devices are created and improved, including memory storage devices memristores. A memristor [1-2] is a new, fourth element of an electrical circuit (after capacitor, inductor, and resistor) that connects magnetic flux and electric charge. However, it’s working principle is not based on either the use of magnetic flux or the storage of charge like a capacitor. Rather, it creates a connection between electrical resistance and charge through chemical mechanisms. They can be used for data storage and processing and possess several key characteristics that are superior to those of conventional data storage units [3]. Despite the advantages over other similar devices, such as fast speed switching, low energy consumption, long-term storage, high ON / OFF resistance ratio, multi-level operation cell, simple structure, low cost, good compatibility with Complementary metal–oxide–semiconductor (CMOS) and manufacturability, there are also some problems for these devices, including memristore
active layer structure, isolation passive elements, size of the device and some issues relating to the integration and reproducibility of parameters.

In this article is considered the improving characteristic parameters of memristor based on HfO$_2$ active layer [4-6]. Also experimented tungsten oxide as an active layer with combination hafnium oxide using different combinations of memristor contact materials.

2. Experimental

Experiments were performed using different materials to create a memristor structure: as active layers in the experiments were used metal and transition metal oxides: 1. WO$_x$; 2. HfO$_2$; 3. WO$_x$ +HfO$_2$; 4. HfO$_2$ + HfO$_x$. In the first three researches as a substrate were used (100), 10 Ω·cm, 2 inch, $p$-type silicon wafers and in the fourth experiment was used 2 inch sapphire wafer 300μm thickness and surface orientation (0006). Prior to the experiments substrate surface was chemically cleaned using standard techniques. Technology forming memristor’s active layers as well memristor’s contacts was reactive magnetron sputtering. Sputtering target was made by 50mm diameter W (99.95%) and Hf (99.9%) materials. Rotary and turbo pump combination was used to get the desired vacuum in the vacuum chamber. The base pressure of the system was less than 10$^{-6}$ torr. All the depositions were carried out at a total pressure of 5 x 10$^{-5}$ torr. The distance between the target and substrates was kept at 45 mm and the substrate temperature was 400°C. Design and morphology of the memristors were made by UV photolithography and are designed in the form of „crossbar” (Figure 1), which allows us to individually investigate each memristor and create a database with the possibility of incorporating it into the microchip in the future. Isolation of individual memristor structures were made by photoresist AZ5214E, which is a good electrical isolation material Figure 2.

![Memristor crossbars](image1.png)

**Figure 1.** Memristor crossbars

![Memristor structure](image2.png)

**Figure 2.** Memristor structure
Memristor's structure were performed in different modes: 1) Si (substrate)+W+WO\textsubscript{x}+W; 2) Si (substrate)+W+HfO\textsubscript{2}+W; 3) Si (substrate)+W+WO\textsubscript{x}+HfO\textsubscript{2}+W; 4) Al\textsubscript{2}O\textsubscript{3} (substrate)+TiN (bottom contact) + (HfO\textsubscript{2}-HfO\textsubscript{x}) (active bilayer) +W (top contact) + Al (wiring contact).

3. Results and Discussion

3.1. Si (substrate)+W+WO\textsubscript{x}+W

Tungsten oxide (WO\textsubscript{x}) was used as the active layer of the memristor and the contacts themselves are tungsten. The resulting structure is: Si (substrate)+W+WO\textsubscript{x}+W. The I-V characteristic is shown in Figure 3.

![Figure 3. Memristor I-V characterization](image)

As can be seen from Figure 3, the memory characteristic does not show and the output current is in the order of milliamperes. It behaves like a conventional resistor with 26 ohm resistance.

3.2. Si (substrate)+W+HfO\textsubscript{2}+W

In other experiments, hafnium oxide (HfO\textsubscript{2}) was used as the active material of the memristor. Memristor structure is Si (substrate)+W+HfO\textsubscript{2}+W, and the I-V characteristic is shown in Figure 4.

![Figure 4. Memristor I-V characterization](image)

\(R_{\text{off}}/R_{\text{on}}=1\)
The I-V characteristic shows a change in resistance at the boundaries of the transition layers (W + HfO$_2$ and HfO$_2$ + W), and the output current is in the order of tens of milliamperes, in contrast to the previous case. The decline of the curve on the negative and positive half-axes of the voltage is unchanged and equals approximately 6 ohms. It means that ratio of high resistance state $R_{\text{off}}$ (device is in the locked condition) and low resistant state $R_{\text{on}}$ (switching mode) is equal to 1 and no memorize properties appear.

3.3 Si (substrate)+W+$\text{WO}_x$+HfO$_2$+W

In this experiment, the materials discussed in the previous two cases were used together, i.e. as an active layer was used tungsten oxide and hafnium oxide: Si (substrate)+W+$\text{WO}_x$+HfO$_2$+W. The result turned out to be different Figure 5.

![Memristor I-V Characterization](image)

Figure 5. Memristor I-V characterization

Figure 5 clearly shows the existence of memorizing properties of the material. The maximum output current in the structure is milliamperes ($3.5 \times 10^{-3}$A). However, the corresponding resistance ratios for the locked and open positions are $R_{\text{off}} / R_{\text{on}} \approx 1.36$. High currents (mA) are mainly due to the large area of contact areas. One of the most important parameters of the memristor is the area of the active layer, because the smaller the area, the smaller the leakage currents. The area of the memristor made with the existing photo mask was $70 \times 10^{-5}$ cm$^2$.

3.4 Si (substrate)+W+$\text{WO}_x$+HfO$_2$+W

In order to reduce the contact area of the memristor active layer on the same structure Si (substrate)+W+$\text{WO}_x$+HfO$_2$+W another photo mask was used, which allowed us to reduce the area by 100 times and made $0.7 \times 10^{-5}$ cm$^2$. The obtained characteristic is given in Figure 6.
As can be seen from Figure 6, the leakage current decreased by two orders ($3 \times 10^{-5}$ A), and the ratio of the corresponding impedances to the closed and open states became $R_{\text{off}} / R_{\text{on}} \approx 5.03$.

3.5 $\text{Al}_2\text{O}_3$ (substrate)$+\text{TiN} + (\text{HfO}_2-\text{HfO}_x)+\text{W}+\text{Al}$

In addition to tungsten contact and tungsten oxide active layer, titanium nitride (TiN) was used as one of the contacts and as an active layer was used HfO$_2$-HfO$_x$ bilayer. The memristore structure was created in the following order: $\text{Al}_2\text{O}_3$ (substrate)$+\text{TiN}$ (bottom contact) $+(\text{HfO}_2-\text{HfO}_x)$ (active bilayer) $+\text{W}$ (top contact) $+\text{Al}$ (wiring contact) Figure 7. The electrical parameters of the obtained structure were measured by I-V characteristic Figure 8.
Figure 8. Memristor I-V characterization

Figure 8 clearly shows the memorization properties of the measured structure. It is also clear seems Memristore’s open and locked positions, and consequently their ratio, have increased to 10.

4. Conclusion
To summarize received outcomes, when is used only tungsten oxide as an active layer no memorize properties appeared in the created structures. In the case of HfO$_2$ layer it seems change in I-V curve characterization, but as previous structure no memorize futures. When is used bilayer of WO$_x$+HfO$_2$ oxides the structure started gain some hysteresis behavior, which is characteristic for memristore, but I-V curve showed high leakage currents. For solving problem regarding to leakage current was reduced the size of active layer area by using different photomask, which gave opportunity to reduce area of active layer by 100 times. As a result the leakage current reduced by two orders and improved the I-V characterization of the memristor structure. Finally, in the last expereminetns described in this article, was used sapphire substrate for more isolation of individual memristors, bilayer of hafnium dopped and undopped active layers and titanium nitride as a bottom contact. Result showed improving the behavior of I-V hysteresis and memristor closed and open states ratio became $R_{off}/R_{on} \approx 10$.

In the future it is necessary to continue experimental work in the direction of reducing size of memristor active area and selection memristive materials and their combination in the memristor structure for achieve high ratio of $R_{off}$ and $R_{on}$.

C-V, XRD and XPS measurement has been done for research memristor active layers electrical and structural properties, but is not included in this work.

Acknowledgment
The authors would like to thank Shota Rustaveli National Science Foundation of Georgia for founding the project (№ AR_18_271) in which frame was made these research.

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