Bipolar resistive switching properties of titanium dioxide thin films deposited by different techniques

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Abstract. A comparative study of bipolar resistive switching in thin films of titanium dioxide, fabricated by different techniques, was carried out by analysis of current-voltage characteristics (I-V). For this purpose metal-insulator-metal (MIM) structures were formed with 60-nm-thick titanium dioxide layer deposited by atomic layer deposition (ALD) or RF magnetron sputtering. Based on the analysis of resistance switching characteristics, it was found that the deposition technique of titanium dioxide thin films influences the reproducibility of high-resistance state (HRS) at cycling measurements, the on-resistance (low resistance state)/off-resistance (HRS) ratio, the average values of SET [switching the resistance from a HRS to a low resistance state (LRS)] and RESET [switching the resistance from LRS to HRS] voltages and the number of resistive switching cycles. The results of study of the thin film topography performed by atomic force microscopy (AFM) suggest that the difference in resistive switching parameters could be caused by structural properties of titanium dioxide layers deposited by different techniques.

1. Introduction

The metal oxide thin films with resistive switching and memory effects (memristive structures) are considered to be a potential elemental base for new components of neuromorphic engineering, enabling a combination both data storage and processing in a single unit [1]. A key design issue in this case is a hardware defined functionality of neural networks providing by the gradient change of resistive properties of memristive elements (in comparison with conventional software defined artificial neural networks) [2]. Among the advantages offered by this approach are reduced power consumption (memristor is a non-volatile memory element), increased data processing speed (due to the fast resistive switching of memristive elements), excellent scalability of memristive devices and their compatibility with Back-End-of-Line (BEOL) fabrication processes [3]. Benefits of memristors would allow developing innovative architecture of artificial neural networks based on emulation of basic operation principles of biological neural networks, including spike-timing dependent plasticity (STDP) and lateral inhibition rules. The potential opportunities for creation the memristor-based circuits for artificial neural networks (ANN) with unsupervised learning have been demonstrated in the recent studies in the field of neurocomputing, development of the brain-machine interface and neuroprosthetics [4-6].

We recently reported multilevel resistive switching in thin-film bilayer MIM structures based on a sequence of two oxide layers (TiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}). A large change in resistance, in the range of seven orders of magnitude, is achieved by applying a relatively small voltage (from 2 to 4 V) to the top electrode of the bilayer structure [7]. The appearance of multilevel resistance states in Pt/TiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}/Pt structures is associated with the modified properties of the Al\textsubscript{2}O\textsubscript{3} layer due to oxygen vacancies drifting in under a bias voltage, while the TiO\textsubscript{2} layer acts as a reservoir of oxygen vacancies. The
possibility of multilevel resistive switching in bilayer MIM structures enables its potential application as an electronic equivalent of a synapse for artificial neural networks. The successful integration of the memristive devices in ANN demands the optimization of its switching characteristics in accordance with the basic requirements of neuromorphic circuits, the main of them is enhancing the multilevel state stability while keeping the simplicity of switching algorithms.

Here we present the experimental results on bipolar resistive switching with memory effect in $\text{TiO}_2$ thin oxide layers, taken as a system responsible for the appearance of multilevel resistance states in Pt/$\text{TiO}_2$/Al$_2$O$_3$/Pt structures, to study the influence of deposition technique on its resistive switching parameters.

2. Materials and Methods
The MIM capacitors with Pt electrodes were prepared with 60-nm-thick TiO$_2$ layer (Fig. 1) as follows: first, a 100-nm-thick SiO$_2$ layer was formed by thermal oxidation on a p-type Si (100) substrate. A 25-nm-thick titanium adhesion layer was then deposited on the SiO$_2$ layer, followed by the deposition of a 50-nm-thick platinum bottom electrode (Pt-BE) by DC sputtering at 150°C. Next, the TiO$_2$ layer was deposited by atomic layer deposition (TFS 200, Beneq) at 150°C by using titanium isopropoxide $\text{Ti(CH}_3\text{CH}_2\text{O)}_4$ and H$_2$O gases in one case, or by RF magnetron sputtering (Qprep 500M, Mantis) of metallic titanium target in an argon/oxygen atmosphere at 150°C in another case. Finally, the 100-nm-thick top platinum electrode (Pt-TE) layers were formed by DC sputtering by using a metal shadow mask. The area of the top electrode was 10$^{-3}$ cm$^2$. The thickness of the titanium dioxide layers in Si/SiO$_2$/Ti/Pt/TiO$_2$ structures was controlled by scanning electron microscopy applied to a cross-section formed by FIB (FEI, Helios NanoLab). Local structural properties of the surface of fabricated titanium dioxide layers were measured at room temperature in ambient, exploring atomic force microscopy technique of Veeco SPM instrument. Commercially available silicon tips were employed for the AFM measurements. To investigate switching of the resistance in the fabricated structures, $I$-$V$ curves were measured by using a Keithley 4200-SCS semiconductor characterization system. The operating voltage was applied to the Pt-TE whereas the Pt-BE was grounded. The resistance of the MIM structure was measured by using a low (0.1 V) dc voltage.

3. Results and Discussion
Let us now briefly describe the morphological peculiarities of the fabricated TiO$_2$ layers and then we go through the analysis of the resistive switching parameters. In Fig. 2a,b the results of surface morphology studies with AFM in contact mode at ambient are shown for titanium dioxide layers deposited by ALD (Fig. 2a) and RF magnetron sputtering (Fig. 2b). Both samples have polycrystalline structure, with average value of the equivalent disk radius of crystallites in the range of tens of nanometers: 19 ± 8 nm (measured by 2054 number of grains) for TiO$_2$ films deposited by ALD and 18 ± 15 nm (measured by 1684 number of grains) for the for TiO$_2$ films deposited by RF magnetron sputtering. Despite of average values of lateral sizes of grains in both types of structures, for films grown with RF magnetron sputtering a broader lateral grain size distribution is observed. Surface roughness of TiO$_2$ films deposited by RF magnetron sputtering have higher RMS roughness in comparison with samples deposited by ALD: 12,5 nm and 6,0 nm accordingly.

Figure 1. Sketch of a Pt/TiO$_2$/Pt structure.
Figure 2. Contact mode AFM images of the TiO$_2$ films surfaces: (a) fabricated by ALD technique; (b) fabricated by RF magnetron sputtering.

The resistivity of the structures in the pristine state is $(8 \pm 5) \times 10^7 \, \Omega \, \text{cm}$ for magnetron sputtered films, and one order of magnitude higher for films prepared by ALD - $(18 \pm 8) \times 10^8 \, \Omega \, \text{cm}$. The experimental $I-V$ curves are nonlinear and symmetrical (regarding polarity of applied bias) for TiO$_2$ films deposited by ALD and nonlinear and a-symmetric for samples prepared with RF magnetron sputtering (Fig. 3).

Figure 3. $I-V$ characteristics of Pt/TiO$_2$/Pt structures in a pristine state (as grown) with TiO$_2$ films fabricated by ALD and RF magnetron sputtering.

To initiate a bipolar resistive switching in both types of structures, a two-step electroforming procedure is required (Fig. 4). It was found experimentally that at the first step, a positive voltage should be applied to the top electrode of the structure. The value of the voltage for the first step of electroforming is higher for the films deposited by ALD due to its higher resistivity. Independently of the sample preparation technique the current compliance was set to $10^{-2}$ A. The second step of electroforming demands a negative voltage application (~2.5 V) to the Pt-TE of the structure and does not require setting the level of current compliance. It was revealed experimentally, that successful electroforming leads to activation of the bipolar resistive switching in TiO$_2$ layers. At the same time after electroforming procedure the resistivity of films deposited by RF magnetron sputtering is one order of magnitude less than for films deposited by ALD.
After electroforming procedure the experimental $I$-$V$ curves remain nonlinear and symmetrical for TiO$_2$ films deposited by ALD and nonlinear and a-symmetric for samples prepared with magnetron sputtering in the voltage range ± 1 V. The analysis of $I$-$V$ characteristics shows that they are linearized in a double logarithmic scale for both types of samples with several characteristic parts ($I$-$U^n$), corresponding to linear and power dependences (with $n > 3$ for a HRS), what is typical for space charge limited current (SCLC) [8]. The SET process [switching the resistance from a HRS to a LRS] for bipolar resistive switching (Fig. 5) for both types of the Pt/TiO$_2$/Pt structure happens when a positive voltage is applied to the Pt-TE. Whereas the RESET process (switching the resistance from a LRS to a HRS) occurs at negative voltage (i.e., counterclockwise switching).

Thin titanium dioxide films deposited by ALD exhibit the next resistive switching parameters determined from experimental characteristics (Fig. 6): the average values of set ($V_{SET}$) and reset ($V_{RESET}$) voltages are $V_{SET} = 2,0 \pm 0,2$ V and $V_{RESET} = -1,1 \pm 0,2$ V, correspondingly; the off-resistance ratio/on-resistance ($R_{OFF}/R_{ON}$) is $3,5 \times 10^3$; the reproducibility of a HRS resistivity ($R_{HRS}$) at cycling measurements is $(6 \pm 2) \times 10^7 \Omega$cm. TiO$_2$ films deposited by RF magnetron sputtering give the next SET of resistive switching parameters: $V_{SET} = 3,3 \pm 0,5$ V and $V_{RESET} = -1,9 \pm 0,5$ V, correspondingly; the $R_{OFF}/R_{ON} = 1,7 \times 10^2$; the reproducibility of $R_{HRS}$ at cycling measurements is $(4 \pm 3) \times 10^6 \Omega$ cm. The number of switching cycles is one order of magnitude higher for the TiO$_2$ films deposited by ALD in comparison with magnetron sputtered TiO$_2$ films.
Figure 6. I-V characteristics of Pt/TiO$_2$/Pt structures with a bipolar resistance switching of TiO$_2$ films fabricated by: (a) ALD; (b) RF magnetron sputtering.

In this way, we conclude that there is a clear difference in the resistive switching parameters of titanium dioxide films deposited by different techniques. Under the same thicknesses, polycrystalline structure and bipolar switching behavior, the TiO$_2$ films grown using an ALD technique show improved switching uniformity (in terms of standard deviation of $V_{\text{SET}}$ and $V_{\text{RESET}}$), one order of magnitude higher $R_{\text{OFF}}/R_{\text{ON}}$ ratio, better stability and reproducibility in cycle-to-cycle resistive switching and more sustainable to cycling-induced degradation.

We attribute the difference in the resistive switching properties of Pt/TiO$_2$/Pt structures with peculiarities of the local film structure. The results of surface morphology studies by AFM suggest that the increasing of the grain boundary density in polycrystalline films, deposited by RF magnetron sputtering. To the first approximation, formation of structural defects (line dislocations and point defects) could mainly be attributed to the density of grain boundaries in the films. Taking into account the difference in the resistivity of the as-grown TiO$_2$ films deposited by different techniques, we may conclude the increased impact of leakage current in films fabricated by RF magnetron scattering.

The results of our previous researches indicates that the dominant mechanism of electron transport is an SCLC in materials with high trap concentrations [9]. Traps are presented by point defects of the film structure. While the transition from the HRS to the SET is associated with the trap-filling limit being reached in the local conductive filamentary area.

Considering the increased values of SET and RESET voltages (determined from the I-V curves) in TiO$_2$ films deposited by RF magnetron sputtering, we may assume that the trap-filling limit is reached at higher values of voltages applied to these films. This, in turn, suggests the increased impact of grain boundary mediated leakage currents in polycrystalline films fabricated by RF magnetron sputtering.

4. Conclusion
In summary, (MIM) structures with 60-nm-thick titanium dioxide layers deposited by ALD and RF magnetron sputtering were fabricated to reveal the influence of deposition technique on the resistive switching behavior. Deposited by different techniques polycrystalline TiO$_2$ films in their pristine state (as grown) have different resistive properties presumably driven by its local structure peculiarities. Under the similar switching behavior, the switching properties of films prepared with ALD technique are far exceed those for structures deposited with RF magnetron sputtering in terms of stability and switching uniformity. These results represent an important step towards the adaptation the unique properties of memristive devices to the requirements of an ANN.

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