Reversible modification of electrical properties at the nanoscale level in bilayer oxide systems

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Abstract. We report the results of experimental study of resistive switching effects in heterogeneous oxide systems based on bilayers with different sequences of two oxide layers (TiO$_2$ and Al$_2$O$_3$) by means of tunnelling atomic-force microscopy (AFM). These systems demonstrate a bipolar resistive switching. Moreover, the resistance state of metal-insulator-metal capacitors with TiO$_2$/Al$_2$O$_3$ bilayers can be electrically tuned over seven orders of magnitude. To elucidate a possible influence of nanoscale characteristics of these bilayers on the parameters of both bipolar resistive switching and electrical tuning of the resistance state, electrical properties of TiO$_2$/Al$_2$O$_3$ bilayers with different thicknesses of the top Al$_2$O$_3$ layer and Al$_2$O$_3$/TiO$_2$ bilayers were investigated. The presence of more conductive anatase crystallites in the amorphous phase of TiO$_2$ layer was experimentally observed only for TiO$_2$/Al$_2$O$_3$ bilayers. Measurements of the current distribution justify the reversible formation of conductive areas in the top Al$_2$O$_3$ layer located directly above the anatase crystallites, under the voltage application between the AFM tip and the bottom electrode of the structure. These conductive areas could be switched back into the high resistive state by application of bias voltage of reverse polarity.

1. Introduction
We have recently reported multilevel resistive switching in thin-film bilayer metal-insulator-metal (MIM) structures based on two oxide layers (TiO$_2$ and Al$_2$O$_3$) combined to form a bilayer structure [1,2]. It has been shown that at certain technological parameters, the resistance of MIM capacitors with TiO$_2$/Al$_2$O$_3$ bilayer structure can be electrically tuned in the range from $10^{12}$ to $10^5$ Ω. To achieve a certain resistance state (resistance level) of the structure in the given range, a pulse of bias voltage (in the range of 2-4 V) is applied between the top and bottom electrodes. The value of applied voltage determines the level of the structure’s resistance: the greater the value of the voltage applied, the smaller the resistance of the TiO$_2$/Al$_2$O$_3$ bilayer after its application. Relative to the given resistance level (set by pulse voltage application) in MIM capacitors based on TiO$_2$/Al$_2$O$_3$ structures, bipolar resistive switching occurs. At the SET process, the resistance of this MIM structure switches from a high resistive state (HRS) to a low resistive state (LRS), whereas the RESET process implies the resistance switches back from a LRS to a HRS. The on-resistance/off-resistance ratio for a certain resistance level of this structure could vary from one to two orders of magnitude depending on the resistance level (Fig. 1).

Unfortunately, until now a stable tuning of the resistance level in MIM capacitors based on TiO$_2$/Al$_2$O$_3$ structures back from low resistance level ($10^5$ Ω) to high resistance level ($10^{12}$ Ω) has not been achieved. The issue of controllable switching between different resistance levels in these structures also remains open. Answers on these questions will largely determine the prospects for application of these bilayers with multilevel resistive switching in the field of non-volatile memory devices.
Figure 1. (a) Tuning the resistance of the Pt/TiO$_2$/Al$_2$O$_3$/Pt structure by pulse voltage application; (b) $I-V$ curves typical for bipolar resistive switching of the Pt/TiO$_2$/Al$_2$O$_3$/Pt structure, seven resistance levels depicted in (a).

The goal of this work is to clarify the specificity of resistive switching effects in MIM structures based on two oxide layers (TiO$_2$ and Al$_2$O$_3$) by means of tunnelling atomic force microscopy (AFM) at the nanoscale level. This investigation was taken with a view to elucidate possible influence of nanoscale characteristics of these heterogeneous oxide systems on the parameters of both bipolar resistive switching and electrical tuning of the resistance level in the given bilayers. We suppose that deeper understanding the nature and mechanism of multilevel resistive switching will allow us to develop a proper algorithm of controllable switching between intermediate levels of the resistance in these structures. Moreover, peculiarities of resistive switching effects studied at the nanoscale level could give ideas on the deviation of electrical behaviour of the resistive random-access memory (characterized by storing data in cells through changing the resistance of thin metal oxide layer), among which is an uncertainty in the value of the RESET voltage [3].

2. Materials and methods

MIM capacitors with Pt electrodes were prepared with TiO$_2$/Al$_2$O$_3$ and Al$_2$O$_3$/TiO$_2$ bilayer structures as follows. First, a 100-nm-thick SiO$_2$ layer was formed by thermal oxidation on a p-type Si (100) substrate. A 10-nm-thick titanium adhesion layer was then deposited on the SiO$_2$ layer, followed by the deposition of a 100-nm-thick platinum bottom electrode (Pt-BE) by DC sputtering. Next, the TiO$_2$/Al$_2$O$_3$ or Al$_2$O$_3$/TiO$_2$ bilayer structures were deposited by atomic layer deposition at 200°C by using trimethylaluminium or tetrakis(dimethylamino)titanium and H$_2$O gases. Post-deposition annealing was done at 200°C for 30 s under ambient oxygen.

The thickness of the titanium oxide layer in both types of bilayer structures was 30 nm, while the thickness of the top aluminium oxide layer in TiO$_2$/Al$_2$O$_3$ bilayer was varied and was equal to 1, 3, and 5 nm for different structures. In case of Al$_2$O$_3$/TiO$_2$ bilayers, the thickness of aluminium oxide layer was 5 nm (Fig. 2).

The Pt top electrode (Pt-TE) layers were formed by electron-beam evaporation by using a metal shadow mask. The area of the top electrode was $10^{-4}$ cm$^2$. Schematically, the structure of formed bilayers is shown in Figure 2.

The bilayer structures thus fabricated were characterized by ellipsometry, electron microscopy, Auger electron spectroscopy, high-energy electron diffraction (HEED), and optical techniques. The ellipsometry results indicate that the thickness irregularity of the thin-deposited oxide films was less than 1% over the 100 nm substrate. Auger spectroscopy was used for stoichiometry and depth profiling element analyses of the TiO$_2$ thin film. The results justify the in-depth TiO$_2$ film homogeneity, the absence of uncontrollable impurity in the film, and the relatively narrow interface regions. The results of optical measurements and HEED indicate that TiO$_2$ in the film is in the anatase phase with presence of amorphous phase in a polycrystalline TiO$_2$ film [2]. The Al$_2$O$_3$ layers less than 5 nm thick have an amorphous structure independent of the technological parameters of film deposition.
Figure 2. Schematics of Pt-BE/TiO₂/Al₂O₃/Pt-TE (on the left) and Pt-BE/Al₂O₃/TiO₂/Pt-TE (on the right) capacitors.

The tunnelling AFM measurements were performed at room temperature using Veeco scanning probe microscope. Commercially available Pt-coated silicon tips were employed for mapping the current distribution over the surface of the thin oxide films. To investigate resistive switching in the fabricated capacitors, I-V curves were measured under ambient condition using Keithley 4200-SCS semiconductor characterization system. The operating voltage was applied to the Pt-TE with the Pt-BE grounded.

3. Results and discussion

Earlier it was shown that the sequencing of titanium oxide and aluminium oxide layers could significantly influence the electrical properties of MIM structures [1]. Pt-BE/Al₂O₃/TiO₂/Pt-TE capacitors demonstrated a stable bipolar resistance switching with on-resistance (at low resistance state)/off-resistance (at high resistance state) ratio of ~10² driven by a relatively small voltage ±0.8 V after forming process. The resistance in HRS was 2×10³ Ω, while in LRS it was 2×10¹ Ω. Pt-BE/TiO₂/Al₂O₃/Pt-TE structures do not demand a forming process, its resistance could be electrically tuned, starting from ~10¹² Ω and up to ~10⁶ Ω, by negative bias application to the top electrode of the structure. Moreover, compared to the “prepared” (by voltage application) level of the structure’s resistance, a stable bipolar resistance switching was observed.

Conductive AFM measurements aim to estimate the possible influence of nanoscale characteristics of bilayers on the parameters of both bipolar resistive switching and electrical tuning of the resistance (in case of Pt-BE/TiO₂/Al₂O₃/Pt-TE capacitors). For this purpose, we scan the surface of bilayers with voltage applied between the conductive AFM tip and the bottom electrode of the structure, registering the topography and the current distribution over the sample’s surface simultaneously. We distinguish two range of voltages applied between an AFM tip and the bottom electrode of structures. First, a reading voltage, the value of which was small enough to ensure that the resistance states remained unchanged during and after scanning the samples. The second one is so-called writing voltage, the value of which could provoke the certain changes in the current distribution (resistance state of the structure) could be associated with resistive switching effects.

The experiment was organized and pursued along the lines indicated below:

1) an area of sample’s surface of 3×3 μm² in size was scanned with reading bias applied between an AFM tip and the bottom electrode of the structure to visualize the initial distribution of the current over the sample’s surface;

2) the same area was then scanned with writing bias, the value of which sweeping in the range of -4V - +6V, to induce the changes in current distribution (resistance state of the structure) could be associated with resistive switching effects;

3) after each scan with writing voltage application, the same surface area was scanned with reading voltage application to register possible changes in current distribution induced by writing voltage application.

3.1. Topography of TiO₂/Al₂O₃ and Al₂O₃/TiO₂ bilayers

The results of topography measurements of TiO₂/Al₂O₃ and Al₂O₃/TiO₂ are shown in Figure 3.

The surface topography of bilayers with top aluminium oxide layer is qualitatively different from the samples with top titanium oxide. Measurements of the TiO₂/Al₂O₃ bilayers visualize the single grains on the topography distributed uniformly over the sample’s surface (Fig. 3a,c). The character of
topography is similar for all TiO$_2$/Al$_2$O$_3$ bilayers independently of the thickness of the top aluminium oxide layer. Statistical analysis of grains made for these type of bilayers justifies that the fraction of grains occupies from 9 to 15 % of the total scan area and may vary slightly from scan to scan. This variation is rather due to the location of the measurements than due to the effect of Al$_2$O$_3$ top layer thickness in different bilayers. An interesting fact is that these grains are distributed almost uniformly both over their height (from 8 to 14 nm) and lateral sizes (mean diameter is approximately 80 nm) for all bilayers (Fig. 3e,f). By supplementing the results of optical and HEED measurements, we consider that these grains are crystallites of anatase phase alternating with amorphous phase (seen as flat areas on the surface topography) in TiO$_2$ layer. The specificity of atomic layer deposition technique implies that the top aluminium oxide layer is an atomically flat, conformal layer. At all given thicknesses, Al$_2$O$_3$ layers have an amorphous structure and should be visualized as a flat surface on the topography. Thus, we can conclude that the only reason for appearance grains on the topography of TiO$_2$/Al$_2$O$_3$ bilayers is an inclusion of anatase phase in TiO$_2$ layer. Further confirmation of this fact follows from the results of measurements of single TiO$_2$ layers (of the same thickness) grown on the bottom platinum electrode and annealed at different temperatures. Increasing the temperature of postdeposition led to decrease in amount of amorphous phase in TiO$_2$ film, according to the results of HEED and AFM measurements of the topography (not shown here). The topography of a single TiO$_2$ layer deposited at the same technological conditions on a bottom platinum electrode was similar to those obtained on TiO$_2$/Al$_2$O$_3$ bilayers.

Meanwhile, the surface topography of bilayers with top titanium oxide layer is atomically flat (Fig. 3b), without grains. This result allows us to conclude that deposited on aluminium oxide layer, TiO$_2$ layer more likely has an amorphous structure in Pt-BE/Al$_2$O$_3$/TiO$_2$/Pt-TE capacitors.

![Figure 3](image)

**Figure 3.** (a) topography of TiO$_2$/Al$_2$O$_3$ (30 nm/5 nm) bilayer’s surface; (b) topography of Al$_2$O$_3$/TiO$_2$ (5 nm/30 nm) bilayer’s surface; (c) topography of TiO$_2$/Al$_2$O$_3$ (30 nm/1 nm) bilayer’s surface (3×3 μm$^2$); (d) statistical grain’s analysis, performed over the 9 μm$^2$ surface area from (b); (e) height profile taken above the area of the topography containing several grains.
3.2. Current distribution over the surface of TiO$_2$/Al$_2$O$_3$ and Al$_2$O$_3$/TiO$_2$ bilayers

The results of measurements of the current distribution over the surface of TiO$_2$/Al$_2$O$_3$ bilayers with the thickness of top aluminium oxide layer equal to 1 nm (Fig. 4a,b) suggest that areas of the samples associated with grains are more conductive. Taking into account the conformity of Al$_2$O$_3$ layer and the fact that at the given thickness this layer has a high transparency for tunnelling current, we can conclude that the contrast in current distribution (observed at scanning with reading voltage) is related to difference in conductivity values of anatase crystallites and amorphous phases of titanium oxide. This is consistent with the fact that the resistivity of undoped titanium oxide is $10^4$–$10^7$ Ω cm, but with the formation of oxygen vacancies related to Ti$^{3+}$, its value reduces to 10 Ω cm for anatase and 100 Ω cm for rutile [4].

With the increase in the thickness of top aluminium oxide layer, the value of measured current through TiO$_2$/Al$_2$O$_3$ bilayers decreases due to the negligible impact of tunnelling current. In this case, the resistance of TiO$_2$/Al$_2$O$_3$ bilayers will be provided by the Al$_2$O$_3$ layer (the resistivity of Al$_2$O$_3$ is $10^{13}$-$10^{15}$ Ω cm as opposed to $10^4$-$10^7$ Ω cm for TiO$_2$). In the initial state, the resistance of the Pt/TiO$_2$/Al$_2$O$_3$/Pt structure is $\sim10^{12}$ Ω. For the system with the thickness of top aluminium oxide layer equal to 3 nm, there was no contrast on current distribution taken at reading values of voltages applied between the AFM tip and bottom electrode. Increasing the value of voltage to -2V leads to a situation, when all areas of aluminium oxide above the crystallites of anatase in TiO$_2$ layer become conductive.

Figure 4. (a) Topography and (b) current distribution over the surface of TiO$_2$/Al$_2$O$_3$ bilayer (30 nm/1 nm) obtained at -1V of bias voltage applied between the conductive AFM tip and the bottom electrode of the structure. (c) Topography and (d) current distribution over the surface of TiO$_2$/Al$_2$O$_3$ bilayer (30 nm/5 nm) obtained at -4V of bias voltage applied between the conductive AFM tip and the bottom electrode of the structure.
Figure 5. Topography (on the left) and corresponding current distribution (on the right) for TiO$_2$/Al$_2$O$_3$ bilayer (30 nm/5 nm) showing the dynamics of reversible formation of stable conductive areas in the top aluminium oxide layer after scanning with voltage applied between the AFM tip and the bottom electrode of the structure.
The most interesting results were obtained on the system with 5-nm-thick top aluminium oxide layer. In this case, the value of bias voltage applied between the AFM tip and the bottom electrode of the structure correlates with the number of conductive areas appeared above the crystallites of TiO$_2$ layer at scanning (Fig. 5). The higher the voltage, the larger number of conductive areas appears at writing voltages. Moreover, a number of conductive areas visualized on a current distribution at scanning with writing voltages also remain conductive at reading voltage. Application of writing voltage of reverse polarity leads to switching previously formed conductive areas back into the high resistance state. Here, it should be mentioned, that $I$-$V$ characteristics with bipolar resistive switching could be measured with AFM tip only in location of previously formed conductive areas. Whereas, in Al$_2$O$_3$/TiO$_2$ (5 nm/30 nm) bilayer, observing resistive switching with $I$-$V$ curves measurements is possible independently on the location of the AFM tip on the surface of the sample.

We consider that the varying number of conductive areas in the top aluminium oxide layer is a reason of instability of the value of both SET and RESET voltages for TiO$_2$/Al$_2$O$_3$ (30 nm/5 nm) bilayers with multilevel resistive switching effects. Here, we would like to clarify why we do not relate an appearance of these conductive areas with formation conductive filaments, a popular model to explain the resistive switching effect in metal oxide structures [5-6]. We explain the appearance of multilevel resistance states in Pt/TiO$_2$/Al$_2$O$_3$/Pt structures by modification of properties of the Al$_2$O$_3$ layer due to oxygen vacancies drifting under a bias voltage. In this case, the TiO$_2$ layer acts as a reservoir of oxygen vacancies. We assume (according to the results of low temperature measurements [2]) that a bipolar resistive switching relatively the given level of resistance happens due to purely electronic processes and is not related to thermal or thermochemical processes. Thus, forming (by one polarity of bias) and erasing (by another polarity) of the conductive areas at scanning the surface of TiO$_2$/Al$_2$O$_3$ with AFM tip highlights once again the possibility to reversible change the conductivity of the Al$_2$O$_3$ layer, which we relate to multilevel resistive states in this structure. An appearance of a certain number of these areas could be explained by the specificity of measuring technique. We obtain a current distribution by scanning (moving) the conductive AFM tip along the surface, i.e. apply voltage locally. Taking into account that the tip-surface contact area does not exceed tens of nanometres in diameter and strongly influencing by topography, it seems reasonable to suspect that conductive areas should appear consequently in places associated with an existence of anatase crystallites in TiO$_2$ layer. If the structure is covered with top Pt electrode, the bias is applied to the whole area underneath the electrode. In this case, conductivity of the Al$_2$O$_3$ layer changes simultaneously and more or less uniformly. Presence of anatase crystallites in TiO$_2$ layer will introduce the instability in the values of SET and RESET voltages.

![Figure 6](image-url)

**Figure 6.** (a) $I$-$V$ curves of Al$_2$O$_3$/TiO$_2$ bilayer and (b) $I$-$V$ curves of TiO$_2$/Al$_2$O$_3$ bilayer measured with AFM tip.
One important remark should also be done here to explain why we do not connect an appearance of conductive areas with common filamentary approach, explaining the bipolar resistive switching in metal oxides. In case of Al₂O₃/TiO₂ (5 nm/30 nm) bilayer we were able to measure the $I$-$V$ characteristics with AFM tip in any place on the surface of top TiO₂ layer (Fig. 6). This bilayer does not exhibit any crystallites (Fig. 3b) in TiO₂ layer, but demonstrates a stable bipolar resistive switching [7]. Thus, we assume that in our case reversible formation of conductive areas in TiO₂/Al₂O₃ bilayers are related to changes in the conductivity of the top aluminium oxide layer of this structure.

4. Conclusion
This paper presents an investigation of Pt/TiO₂/Al₂O₃/Pt and Pt/Al₂O₃/TiO₂/Pt bilayers by means of tunnelling atomic force microscopy. The presence of more conductive anatase crystallites in the amorphous phase of TiO₂ layer was experimentally observed only in Pt/TiO₂/Al₂O₃/Pt bilayers. Scanning with bias applying between the AFM tip and the bottom electrode of these structures leads to reversible formation of conductive areas in the top aluminium oxide layer located directly above the anatase crystallites. These conductive areas could be switched back into the high resistance state by application of bias voltage of reverse polarity. Fraction of the conductive area of the sample varies with the value of applied bias between the tip and the bottom electrode of the sample. We consider an appearance of conductive areas in TiO₂/Al₂O₃ bilayers with the possibility to reversibly change the conductivity of the Al₂O₃ layer, which we relate to multilevel resistive states in these structures. Nevertheless, the presence of heterogeneity at the nanoscale level (owing to the anatase crystallites) in Pt/TiO₂/Al₂O₃/Pt structures could influence on the stability of the parameters of both bipolar resistive switching and electrical tuning of the resistance in these heterogeneous oxide systems.

In Pt/Al₂O₃/TiO₂/Pt capacitors, TiO₂ is amorphous (grown on the Al₂O₃ layer). Both Pt/TiO₂/Al₂O₃/Pt and Pt/Al₂O₃/TiO₂/Pt structures demonstrate a bipolar resistive switching on $I$-$V$ characteristics measured with AFM tip located on the surface of the top layer of given bilayers.

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