Transparent-conductive-oxide (TCO) buffer layer effect on the resistive switching process in metal/TiO$_2$/TCO/metal assemblies

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Abstract
The effect of a transparent conductive oxide (TCO) buffer layer on the insulator matrix and on the resistive switching process in the metal/TiO$_2$/TCO/metal assembly was studied depending on the material of the TCO (ITO-($\text{In}_2\text{O}_3$)$_{0.9}$(SnO$_2$)$_{0.1}$ or SnO$_2$ or ZnO). For the first time electro-physical studies and near edge x-ray absorption fine structure (NEXAFS) studies were carried out jointly and at the same point of the sample, providing direct experimental evidence that the switching process strongly influences the lowest unoccupied bands and the local atomic structure of the TiO$_2$ layers. It was established that a TCO layer in a metal/TiO$_2$/TCO/metal assembly is an additional source of oxygen vacancies for the TiO$_2$ film. The $R_L$ ($R_{H}$) states are achieved presumably with the formation (rupture) of the electrically conductive path of oxygen vacancies. Inserting an Al$_2$O$_3$ thin layer between the TiO$_2$ and TCO layers to some extent restricts the processes of migration of the oxygen ions and vacancies, and does not allow the anti-clockwise bipolar resistive switching in a Au/TiO$_2$/Al$_2$O$_3$/ITO/Au assembly. The greatest value of the ratio $R_{H}/R_L$ is observed for the assembly with a SnO$_2$ buffer layer that will provide the maximum set of
intermediate states (recording analog data) and increase the density of information recording in this case.

Keywords: resistive switching, transparent-conductive-oxide, NEXAFS, $I-V$ characteristics, oxygen vacancies, buffer layer

1. Introduction

The relentless downsizing of microelectronic devices has already brought the size of their critical parts to the range of few nanometers, and continues to challenge scientists and technologists. Developing nanoscale memory-bit cells [1, 2] for non-volatile random access memory (NVRAM) is now a key technological step. Among the many candidates for next-generation non-volatile memory based on a non-charge mechanism, resistance-switching random access memory (ReRAM) has attracted attention as an essential step towards a new era of non-Boolean neuromorphic computing [3, 4]. The main idea of ReRAM connects with the creation of a passive circuit element memristor (the short name of a memory resistor) [5–7]. As follows from [5], the memristor with memristance $M$ provides a functional dependence between flux $\phi$ and charge $dq = M dq$. In the special case when $M$ is itself a function of the charge, in other words, the resistance of the material depends on the charge passing through it, and new circuit functions such as resistive switching are opened.

The mechanism of resistive switching and charge transport is still under debate. In the review [8] three different types of resistive switching (an electrochemical metallization mechanism, a valence change mechanism, and a thermochemical mechanism) are described. The valence change mechanism occurs in binary oxides and perovskite oxides and is triggered by the migration of oxygen anions. The change of the stoichiometry is expressed by a valence change of the cation sublattice and as a consequence leads to a change in the electronic conductivity. In the thermochemical mechanism a change of stoichiometry occurs due to a current-induced increase of the temperature. The electrochemical metallization mechanism relies on an electrochemically active electrode metal.

Many binary transition metal oxides [7–15] as well as multinary oxides with at least one transition metal sublattice [8, 16–18] show resistive switching. The oxide-based elements demonstrate high speed switching, with the possibility of obtaining intermediate resistance values and sufficiently stable multilevel switching. The observed resistive switching in such elements occurs due to the presence in these materials with various defects and impurities which alter the electron transport in the material. Titanium oxide is considered as the most promising switching material [19–21] due to the existence of a continuous homologous series of oxides of TiO to TiO$_2$, the existence of thermal–chemical switching modes [22] and a minimal value of switching time (5 ns) [23]. Note that to provide a switching control of such elements it is necessary to create defects in materials, either during or after fabrication of the element through the electric field effect on the pristine structure (electroforming process) [8].

It has been established in [24–26] that inserting a thin buffer layer between the substrate and dielectric film affects the self-organization and the properties of the active layer. Taking into account a high concentration of oxygen vacancies in transparent conductive oxide (TCO) films, one can assume that TCO layers in the metal/TiO$_2$/TCO/metal assembly will be an additional source of oxygen vacancies for the TiO$_2$ film. Earlier we revealed that such
assemblies demonstrate the memristor’s effect after synthesis (without additional annealing) and that allows progress toward understanding the nature of the memristor effect. Also it was established that after the switching process these structures can be retained for a long time.

In view of this, the goal of the current paper is a study of the effect of TCO buffer layers on the insulator matrix in the metal/TiO$_2$/TCO/metal assembly and on the resistive switching process. In order to gain insight into the electronic structure of the TiO$_2$ film, for the first time electro-physical studies and x-ray spectroscopic investigations were carried out jointly. NEXAFS (near-edge absorption fine structure) spectroscopy is one of the effective techniques for study of the electronic atomic and crystalline structure of materials. The x-ray absorption process has a local character (associated with hole localization in the core–shell) and dipole selection rules for the transitions between the initial and the final states have been worked out. Thus the possibility of obtaining information about local and partial density of electronic states of the conduction band is realised.

2. Experimental details

TiO$_2$ films of 20–80 nm thickness were grown by the atomic layer deposition (ALD) technique on top of production-grade substrates (Ni or glass). ALD synthesis provides the thickness-control and aggressive conformality of TiO$_2$ thin films at a reasonably low processing temperature.

The uniform transparent conductive oxide (TCO) buffer layer (ITO ((In$_2$O$_3$)$_0.9$(SnO$_2$)$_{0.1}$, SnO$_2$, or ZnO) was used and grown on a substrate prior to the ALD of TiO$_2$ film. The TiO$_2$ films were deposited in a cross-flow ‘Nanoserf’ reactor at a temperature of 200 °C using TiCl$_4$, Ti(OCH(CH$_3$)$_2$)$_2$, [(CH$_3$)$_2$N]$_4$Ti and H$_2$O as precursors.

The resistive switching behavior of the synthesized structures was measured at room temperature using an original setup in the $I$–$V$ sweep mode (figure 1). The $I$–$V$ curves of the sample were measured by applying a linearly varying current in the range of +/-10 mA to the top electrode, with the bottom electrode grounded. As for the ohmic contact to the TiO$_2$ and TCO layers, Cu, Au or Pt circular-shaped electrodes were used as external point contacts. The contact area was about $3 \times 10^{-3}$ cm$^2$. The voltage drop across the sample was changed to within +/-10 volts with increments of 12 mV, and that allowed the creation of an electric field of the order of 1 MV cm$^{-1}$ in the TiO$_2$ layer. The experimental error connected with the computer extrapolation of the data in the region of zero current at zero voltage was about 25 mV. The used setup also allowed registering a capacity (at 1 MHz ac) of the studied structures.

Figure 1. Circuit diagram of electrophysical measurements.
The quality of the synthesized structures was controlled by scanning electron microscopy (SEM), a scanning ion microscope (SIM) and x-ray microanalysis. It was established for all the films that the thickness uniformity was better than 0.3 nm across the wafer.

The near edge x-ray absorption fine structure (NEXAFS) measurements were performed at the reflectometer set-up mounted on the optics beamline (D-08-1B2) at the Berlin Synchrotron Radiation facility BESSY-II of the HZB. A GaAsP diode, together with a Keithley electrometer (617), was used as a detector. NEXAFS spectra were measured at the incident angle of 45° in the vicinity of Ti L2,3- and OK-absorption edges with an energy resolution of better than E/ΔE = 3000. The spectra were obtained by monitoring the total electron yield from the samples in a current mode.

A special fiducial grid was developed and tested, and applied on the surface of the samples, enabling measurement of the current–voltage and spectroscopic studies at the same point of the film. The apertures were also used to minimize the cross-section of the x-ray beam and thus to narrow the area of the light spot on the film to a size comparable with the Au electrode contact area. As a consequence, the obtained NEXAFS spectra provided information on changes in the electronic atomic structure itself from the electric field impact area.

3. Results and discussion

It is already known [8, 10, 18, 27, 28], in the case of a single oxide layer structure (unlike bilayer structures consisting of non-stoichiometric oxide and oxide) the electroforming step of the pristine structure is required before bistable switching is achieved. Often, the electroforming is a somewhat slower process than the actual switching. In point of fact, electroforming is the soft breakdown of the insulating oxide layer when the high electric field is applied to the structure. When a high electric field is applied, the oxygen atoms are knocked out from the lattice and move to the electrode with the positive voltage, creating defects that lead to the formation of levels in the band gap [29–33].

The impact of a strong electric field of the order of 1 MV cm⁻¹ on the metal/TiO₂/TCO/metal structures was carried out by applying a negative bias to the top electrode (with the bottom electrode grounded) with an appropriate compliance current that leads to a decrease in the initial resistance \(R_0\) of the pristine structure (after synthesis) to \(R_H\), which we will refer to as a high-resistance state \((R_H)\).

3.1. Current (I)–voltage (V) studies of metal/TiO₂/TCO/metal assemblies

Figure 2(a) shows I–V curves for the Au/TiO₂(20 nm)/SnO₂/Au assembly. For this structure the initial resistance \(R_0\) was reduced from \(R_0 = 50 \text{kΩ} \) to \(R_H = 5–10 \text{kΩ} \) after the electroforming step. The measurements reveal that the asymmetric I–V loops with non-linear rectifying features follow the voltage sweep \(0 \rightarrow V_{\text{min}} \rightarrow 0 \rightarrow V_{\text{max}} \rightarrow 0\) in sequence, as shown by the arrows. Detailed analysis of the switching process in a metal/TiO₂(20 nm)/SnO₂/metal assembly shows that resistive switching from one state to another state in this structure occurs only by changing the polarity of the applied voltage (only by applying a negative bias for \(R_H \rightarrow R_L\) switching and only by applying the positive bias for \(R_L \rightarrow R_H\) switching) and under conditions of a strong electric field applied to the TiO₂ layer (\(\sim 1 \text{ MV cm}^{-1}\)). An increase in the absolute value of the bias potential reaches a certain threshold value above which the structure transfers from the \(R_L\) state into the \(R_H\) state (or some intermediate states) and vice versa. The multiple resistive states
realized in the structure and characterized by different values of the resistance for the Au/TiO\(_2\)(20 nm)/SnO\(_2\)/Au structure are shown in figure 2(b). The observed deviation from the zero current at zero voltage (figure 2(b)) may be related to the nanobattery effect as reported by [34]. However, the value of the observed deviation (about 25 mV) is comparable to the experimental error, and computer extrapolation of the data in the region of zero voltage does not confirm or refute the suggested supposition. Controlling the magnitude of the charge flowing through the structure during the process of resistive switching, one can discretely change the value of the resistance. It was established that transition from the high resistance state \(R_H\) to the low resistance state \(R_L\) occurs much faster, i.e. \(\tau_H \rightarrow L \ll \tau_L \rightarrow H\) and was accompanied by an increasing capacitance of the structure by half. The capacitance value remained virtually unchanged within the linear part of the \(I-V\) curve. Thus the formed structure turned out to be capable of storing the \(R_H\) state for a long time, or changes the value of resistance (increase of the slope of the \(I-V\) linear part curves) up to values of the order \(R_L = 250 \Omega\), depending on the charge passing through the structure. We will refer to this state as a low resistance state with \(R_L\). Changes of the resistance value in the region of the linear part of the \(I-V\) curve (change of the slope of the \(I-V\) linear part curves) was reversible, and transition from the state with \(R_L\) to the state with \(R_H\) was accompanied by the occurrence of a charge in the order of \(3 \times 10^{-2} \text{ C}\).

The dependences of the resistance \(R_L\) and \(R_H\) on the electrode material are illustrated in figure 3 on an example of the metal/TiO\(_2\)(20 nm)/SnO\(_2\)/metal assembly. It was established that the \(R_L\) is independent of the electrode material that leads to the conclusion that in the \(R_L\) state the conductivity of the structure is completely determined by the charge carriers transport on the conducting paths in the TiO\(_2\). As opposed to \(R_L\), the resistance value \(R_H\) depends on the electrode material used: the maximum resistance value \(R_H\) was observed in the case of Pt electrodes.
Since the influence of moisture on the resistive switching process has been pointed out by [35], and especially the influence of different electrode materials on the OFF state resistance, and ionic concentration in the presence of moisture [36], we have also carried out additional studies using a special hermetic box filled with nitrogen. It was established that the composition of the atmosphere where the measurements are carried out and the presence/absence of moisture have no effect on the discussed resistive switching or on its characteristics (switching voltage, the resistance values of $R_L$ and $R_H$ states, etc). Based on this observation and the fact that TCO is an additional source of oxygen vacancies we can suppose that the conductivity in the $R_L$ state is due to the formation of conducting filaments composed by oxygen vacancies rather than mobile metallic cations as in the case of Cu/SiO$_2$/Pt [35], for which the influence of moisture is critical.

Also the resistive switching behavior in the Au/TiO$_2$(20 nm)/SnO$_2$/Au assembly by the way of influence on the structure was studied. It was established that the number of switches between different states depends strongly on the method used. As follows from figure 4(a), while continuously measured $I$–$V$ (continuous application of a linearly varying bias voltage)

![Figure 3](image1.png)

**Figure 3.** Dependence of the resistance $R_L$ (a) and $R_H$ (b) on the electrode material for the metal/TiO$_2$(20 nm)/SnO$_2$/metal assembly.

![Figure 4](image2.png)

**Figure 4.** Dependence of the $R_L$ and $R_H$ states on the number (N) of resistive switching in the Au/TiO$_2$/SnO$_2$/Au assembly obtained by: (a) continuously applying a linearly varying bias voltage, (b) applying the current pulse.

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Also the resistive switching behavior in the Au/TiO$_2$(20 nm)/SnO$_2$/Au assembly by the way of influence on the structure was studied. It was established that the number of switches between different states depends strongly on the method used. As follows from figure 4(a), while continuously measured $I$–$V$ (continuous application of a linearly varying bias voltage)
characteristics, only 10–20 complete switching cycles ($R_L \rightarrow R_H \rightarrow R_L$) were observed. When applying the current pulse, a much larger number of complete cycles of switching (figure 4(b)) were achieved, and, most importantly, degradation of the sample was not observed in this case. The obtained resistive states persist for at least 60 h.

Analogous conclusions have been made in the study of a Au/TiO$_2$(30 nm)/ZnO/Au assembly. I–V characteristics for a Au/TiO$_2$(30 nm)/ZnO/Au assembly are shown in figure 5.

The I–V curves of Au/TiO$_2$(25 nm)/ITO/Au assemblies without/with an Al$_2$O$_3$ layer inserted between the TiO$_2$ and ITO layers are shown in figures 6 and 7. The joint analysis of I–V characteristics of all the studied assemblies reveals the possibility of implementing anti-clockwise bipolar resistive switching only in the Au/TiO$_2$/ITO/Au assembly. It is important that insertion of a thin Al$_2$O$_3$ layer between the TiO$_2$ and ITO layers does not realize anti-clockwise bipolar resistive switching.

Figure 5. I–V characteristics of a Au/TiO$_2$(30 nm)/ZnO/Au assembly (arrows indicate the direction of the circuit, colored arrows correspond to transition between resistive states) showing clockwise bipolar resistive switching.

Figure 6. I–V characteristics of a Au/TiO$_2$(25 nm)/ITO/Au assembly (arrows indicate the direction of the circuit, colored arrows correspond to the transition between resistive states) showing clockwise bipolar resistive switching (a) and anti-clockwise bipolar resistive switching (b).
Summing up the results of current–voltage analysis, let us turn to figure 8 where the average $R_H/R_L$ ratio for all of the studied assemblies is shown. One can see that the greatest value of the ratio $R_H/R_L$ is observed for the assembly with a SnO$_2$ buffer layer. From the viewpoint of practical use of memristor memory, this means that it is possible to implement the maximum set of intermediate states (recording analog data), and increases the density of information recording in this case. That is what gives preference to the SnO$_2$ sublayer.

Based on the obtained set of current ($I$)–voltage ($V$) results, we tried to make preliminary conclusions about the possible mechanisms of the resistive switching process. As was mentioned above, the electroforming step of the pristine structure is required before bistable switching is achieved. The electroforming process is accompanied by formation of the levels in the band gap (the appearance of an additional conduction channel due to the formation of electronic states in the band gap of the insulator). As a result, the conductivity of the structure in the $R_H$ state is defined by two processes: conductivity by these levels; and conductivity by the conduction band on the Schottky-like transport mechanism. This is evidenced by reducing the impact of emissions through the Schottky-like barrier at the TiO$_2$–metal interface, increasing the work function of the electrode used (figure 3(b)).

![Figure 7. I–V characteristics of a Au/TiO$_2$(25 nm)/Al$_2$O$_3$(5 nm)/ITO/Au assembly (arrows indicate the direction of the circuit, colored arrows correspond to transition between resistive states) showing clockwise bipolar resistive switching.](image1)

![Figure 8. Average $R_H/R_L$ ratios for studied assemblies.](image2)
The independence of the resistance $R_L$ on the electrode material i.e. work function (figure 3(a)) allows us to suggest that in the $R_L$ state the conductivity of a structure is completely determined by the charge carrier transport in the levels in the band gap of TiO$_2$. Such an assumption agrees well with [37]. According to [37], the formation of complexes containing oxygen vacancies: $(\text{Ti}^{3+} - \text{V}_o + 2e)^0$ and $(\text{Ti}^{3+} - \text{V}_o^* + 1e)^+$ is typical for TiO$_2$ layers. Such complexes lead to the formation of energy levels in the band gap located at $\sim 0.3$ eV and $\sim 0.5$ eV below the bottom of the conduction band [37]. It is plausible to associate the $R_L$ state of the structure with the presence of the maximum concentration of the oxygen vacancies in the TiO$_2$ layer, which may form conductive paths of oxygen vacancies, so-called conductive filaments. A significant increase in the resistance of the structure (from $\sim 10\,\Omega$ to $\sim 100\,k\Omega$) after annealing in an oxygen atmosphere is additional proof of our assumption. Taking into account:

i) a significant difference in the switching process in the chain $R_H \rightarrow R_L \rightarrow R_H$; ii) a remarkably different inertia of the processes $\tau_L \rightarrow \tau_L \ll \tau_H$; and iii) a different behavior of the intermediate states, it is reasonable to assume that the increase (transition $R_H \rightarrow R_L$) and reduction (transition $R_L \rightarrow R_H$) of conductance occur due to different mechanisms.

### 3.2. NEXAFS study of Au/TiO$_2$/ITO/Au and Au/TiO$_2$/Al$_2$O$_3$/ITO/Au assemblies

The absorption spectra in the vicinity of titanium L$_{2,3}$- and oxygen K-absorption edges were measured for all samples with an ITO ((In$_2$O$_3$)$_{0.9}$(SnO$_2$)$_{0.1}$) TCO buffer layer. It should be noted that the Ti L$_{2,3}$- absorption spectra for all of the studied samples (before and after switching) were almost indistinguishable, and corresponded to the spectrum of the amorphous TiO$_2$ film. That means that the main changes of the structure occur in the sublattice of oxygen. Therefore only the OK-absorption spectra will be discussed further.

Figure 9 shows the OK-absorption spectra of the studied films (pristine structure). The relative intensities of all spectra have been normalized to the continuum jump (at the photon energy of 560 eV for O1s absorption spectra) after subtraction of a sloping background, which was extrapolated from the linear region below the O1s absorption onset. Such normalization provides about the same total oscillator strength for all of the O1s-absorption spectra over the photon energy range of 520–560 eV, in accordance with a general idea of oscillator strength distribution for the atomic x-ray absorption [38]. It is important to emphasize that all of the
samples were studied at different points of the structure. It was established that for each sample within the statistical error (in the order of 3%), the spectra measured at different points on the surface of the sample coincided.

According to [39–40] the molecular orbitals of TiO₂ derived from a linear combination of atomic orbitals (LCAO) are characterized by four unoccupied orbitals: 2t₂g(Ti 3d + O 2pπ); 3e₃g(Ti 3d + O 2pσ); 3a₁g(Ti 4s + O 2p); and 4t₁u(Ti 4p + O 2p). In TiO₂, all four molecular orbitals are completely empty. In this classification the OK-edge features (labeled as a, b, c and d) can be assigned to one electron transitions from the O 1s orbital to the 2t₂g, 3e₃g, 3a₁g and 4t₁u orbitals of TiO₂, respectively. Thus a and b peaks reflect the core-electron transitions in the oxygen atoms to the lowest unoccupied Ti 3d-t₂g and 3d-e₃g electronic states that are mixed with the 2p states of the ligand (oxygen) atoms. As follows from figure 9, the spectra for all of the studied films correlate well in number and energy position of the main details of the structure. Analysis of the energy position of the peaks shows that within the experimental accuracy (10 meV) the energy separation between a and b peaks ΔEₐ₋ₜ=2.2 eV is close to the value for the amorphous TiO₂ (2.3 eV) [41–42]. At the same time, the appreciable decrease of the main band integral intensity (including a and b peaks) depending on the material of the buffer layer, is traced and is likely to be a result of the varying oxygen content in the synthesized TiO₂ films. As follows from figure 9, the lowest intensity of this band occurs in the film grown onto an ITO layer and is likely to be a result of the formation of the film with the lowest stoichiometry during synthesis, due to the migration of oxygen ions from the TiO₂ film into ITO since the structure of ITO contains a considerable number of oxygen vacancies [43]. Additional evidence of this conjecture can be found in the second band characterized by c and d peaks and related to transitions into the empty electronic states with mixed Ti 4s, 4p + O 2p character. Analysis of the O K-absorption spectra [41–42, 44–47] points to significant differences of the features at higher energies for different crystal modifications and amorphous phases of TiO₂. The less pronounced splitting of the c and d peaks confirms the lowest stoichiometry of the film grown onto ITO buffer layer. The use of the Al₂O₃ blocking layer allows the restriction to some extent of the processes of migration of oxygen ions and vacancies as follows from work [48, 49]. This fact agrees well with our results since the main band integral intensity has a higher value, and more pronounced splitting of the c and d features is traced in the spectrum of the TiO₂/Al₂O₃/ITO assembly (figure 9) as compared with the TiO₂/ITO assembly. Figure 10 demonstrates the OK-absorption spectra of the TiO₂/ITO and TiO₂/Al₂O₃/ITO assemblies before (pristine structure) and after resistive switching. As can be seen from figure 10, the main band integral intensity is appreciably changed after switching that can be related with changes in the sublattice of oxygen. In the case of the TiO₂/ITO assembly (figure 10(a)), the main band integral intensity is increased, and features c and d become more distinguishable for both RH and RL states. This can presumably be related with some restoration of stoichiometry of the TiO₂ film after the resistive switching, due to the reverse migration of oxygen ions from ITO that may be launched under the influence of local heating in the area of high electric field. The effect of the migration of oxygen ions from ITO can be overlapped with effects related directly with the process of resistive switching (the spectra for RH and RL states are almost indistinguishable with a slight predominance of the main band integral intensity for RL state). In this connection, the analysis of the OK-absorption spectra of a TiO₂/Al₂O₃/ITO assembly can give more direct information about the process of resistive switching since a buffer layer of Al₂O₃ considerably restricts the migration of oxygen as mentioned above.
It can be seen from figure 10(b) that the forming process and irreversible conversion of TiO$_2$ film from the $R_0$ to $R_H$ state in the TiO$_2$/Al$_2$O$_3$/ITO assembly is accompanied by a decrease of the main band integral intensity of the OK-absorption spectrum, and the splitting of features $c$ and $d$ becomes less pronounced. This can be related to a general reduction of stoichiometry of the TiO$_2$ film, and the formation of scattered oxygen vacancies that lead to the formation of energy levels in the band gap. The transition of the film into a conductive state is accompanied by a further decrease in the main band integral intensity of the OK-absorption spectrum. In our opinion, the transition $R_H \rightarrow R_L$ is caused by the formation of a conductive path formed by oxygen vacancies in the TiO$_2$ film in the area of localization of high electric field as a result of the thermal ejection of oxygen ions from regular bonding. The electric field violates the symmetry of the potential barrier and reduces its height in the direction of the field on the Schottky-like mechanism that additionally facilitates ejection of oxygen ions from the regular bonding. The negative polarity of the applied voltage at the $R_H \rightarrow R_L$ transition provides displacement of the oxygen ions from the region of the localization of produced vacancy, excluding the possibility of reuptake. In essence, the joined effect of local heating and electric field disturbs the balance between the release of oxygen ions and their reuptake. In this case, an increase in conductivity of the structure is presumably associated with the formation of filaments of the oxygen vacancies. Since the reuptake of oxygen ions is significantly impeded, it is unlikely to expect even a short-term reduction in the conductivity that correlates well with the rapid character of the $R_H \rightarrow R_L$ transition observed in the experiment (figure 6(a)).

For conducting an $R_L \rightarrow R_H$ transition, it is necessary to break the conducting pass formed by oxygen vacancies and reduce a general number of vacancies that correlates with the increased main band integral intensity for the $R_H$ state as compared with $R_L$ state (figure 10(b)). This requires the implementation of more complex and combined processes consisting of the shipping and/or formation of oxygen ions in the region of the conductive path localization (or complexes described above) with its subsequent capture, forming regular (maybe distorted) Ti–O bonding. At least two stages of the process significantly increase its inertia. The slowest step in this case is the formation of oxygen ions in the region of the oxygen vacancies localization. Moreover, this process not just can, but must be accompanied by a process of

Figure 10. The OK-absorption spectra of the TiO$_2$/ITO (a) and TiO$_2$/Al$_2$O$_3$/ITO (b) assemblies after $R_H \rightarrow R_L$ transition (2) (negative polarity of applied voltage) and $R_L \rightarrow R_H$ transition (3) (positive polarity of applied voltage) compared with OK-absorption spectra of the pristine structures (1).
vacancy formation described above, as occurs in conditions of the joint action of the electric field and local heating. This was observed in the short-term fluctuations of the conductivity of the system for certain values of the electric field, established in the experiment (figure 6(a)).

The local heating process at this stage plays a dual role. On the one hand, it can promote the increase in the concentration of oxygen ions due to diffusion and this is a positive factor. On the other hand, the self-heating process initiates the formation of oxygen vacancies, which in this case is a negative factor.

The schematic diagrams shown in figures 11(a)–(c) and 12(a)–(c) summarize the mechanism of conductivity modulation during resistive switching in the TiO$_2$/ITO and TiO$_2$/Al$_2$O$_3$/ITO assemblies. Figures 11(a) and 12(a) illustrate the state of the pristine structure. As was mentioned above, the TiO$_2$ film grown onto the ITO buffer layer is characterized by the lowest stoichiometry compared with the film prepared onto the Al$_2$O$_3$/ITO buffer layer. Taking into account that the ITO layer contains a surplus of the oxygen vacancies [43] (white circles), it is reasonable to assume that the O$^{2-}$ ions (green circles) will easily move from TiO$_2$ into the

Figure 11. Schematic diagram of the conduction mechanism in the TiO$_2$/ITO assembly: (a) pristine structure; (b) formation of conducting path $R_H \rightarrow R_L$; (c) rupture of conducting path $R_L \rightarrow R_H$. Solid arrows show the movement of oxygen ions (green circles). Dotted arrows show the movement of oxygen vacancies (white circles). The thickness of the arrows indicates that the intensity is proportional to the flow quantity.

Figure 12. Schematic diagram of the conduction mechanism in the TiO$_2$/Al$_2$O$_3$/ITO assembly: a) pristine structure; b) formation of conducting path $R_H \rightarrow R_L$; c) rupture of conducting path $R_L \rightarrow R_H$. Solid arrows show the movement of oxygen ions (green circles). Dotted arrows show the movement of oxygen vacancies (white circles).
ITO layer within the interface region, under the influence of the internal electric field (this process is indicated by solid arrows). Al₂O₃ acts as a barrier layer against arbitrary migrations of charged particles [48, 49].

Figure 11(b) illustrates the state of the TiO₂/ITO assembly when a negative bias is applied to the top electrode and the bottom electrode is grounded. In this case, the O²⁻ ions penetrate through the barrier at the TiO₂/ITO interface into the ITO layer leaving behind vacancies. The oxygen vacancies in the ITO side serve as trap sites for the O²⁻ ions (dotted arrows). Simultaneously, there is a process of reverse migration of O²⁻ ions from ITO under the influence of the local heating (thick solid arrows). As a result, the low resistance state \( R_L \) (characterized by high conductivity) is achieved with the formation of electrically conductive paths presumably formed by oxygen vacancies (dotted lines) which are surrounded by oxygen ions from ITO. The electric field (negative polarity applied to the top electrode onto the TiO₂ film) prevents the merging of oxygen ions and vacancies. When positive bias is applied to the top electrode and reaches certain threshold value, the state of the high resistance \( R_H \) is realized (figure 11(c)). O²⁻ ions get trapped in the ITO layer moving back towards the TiO₂ film, which leads to a rupture of the conduction channel in the vicinity of the interface, and oxygen vacancies are again distributed in the ITO layer. It is worth noting that the removal of a small amount of O²⁻ ions is sufficient to break the conduction path and thereby increase resistance.

Similar processes occur during the resistive switchings in the TiO₂/Al₂O₃/ITO assembly (figure 12(b)–(c)). But in this case, the Al₂O₃ prevents a spontaneous movement of the oxygen ions and vacancies in the absence of the electric field, and regulates their movement when the high electric field is applied. The introduction of the Al₂O₃ buffer layer allows the increase of the temporal stability of the \( R_L \) and \( R_H \) states of the film [48]. In the \( R_L \) state the reverse migration of the O²⁻ ions from the ITO layer into the film is prevented by the alumina barrier. O²⁻ ions drift towards the ITO leaving behind vacancies under a negative electric field (figure 12(b)). The reverse migration of O²⁻ ions from ITO into the film is prevented by the alumina barrier. So, the concentration of oxygen in the TiO₂ film decreases, as evidenced by a decrease in intensity of the details \( a-b \) in the OK-edge of the absorption spectrum (figure 10(b)).

4. Conclusion

As was mentioned in the introduction, the use of a thin buffer layer between the dielectric film and substrate affects the self-organization of the film. Taking into account a high concentration of oxygen vacancies in the transparent conductive oxide (TCO) layers we have assumed that the TCO layer in a metal/TiO₂/TCO/metal assembly could be an additional source of oxygen vacancies for the TiO₂ film. In this connection the metal/TiO₂/TCO/metal assemblies were synthesized. The resistive switching process has been studied in the metal/TiO₂/TCO/metal assemblies depending on the material of the TCO (ITO ((In₂O₃)₀.₉(SnO₂)₀.₁ or SnO₂ or ZnO). For the first time, the current work combines both electro-physical studies and x-ray near-edge absorption fine structure (NEXAFS) investigations. It was established that the switching process strongly influences the lowest unoccupied bands and the local atomic structure of the TiO₂ layers. It was established that a TCO layer in metal/TiO₂/TCO/metal assemblies is an additional
source of oxygen vacancies for TiO$_2$ film. The $R_L$ ($R_H$) states are achieved with the formation (rupture) of electrically conductive paths of oxygen vacancies. The resistive switching leads to some restoration of stoichiometry of the film in the TiO$_2$/ITO assembly. A clockwise and anti-clockwise bipolar resistive switching is realized only in the Au/TiO$_2$/ITO/Au assembly. The insertion of the Al$_2$O$_3$ thin layer allows the restriction to some extent of the processes of migration of oxygen ions and vacancies, and does not realize anti-clockwise bipolar resistive switching. The greatest value of the ratio $R_H/R_L$ is observed for assemblies with a SnO$_2$ buffer layer. It was established that a remarkably different inertia is characteristic for increase (transition $R_H \rightarrow R_L$) and reduction (transition $R_L \rightarrow R_H$) of conductance $\tau_H \ll \tau_L \rightarrow H$. Applying the current pulse provides a much larger number of complete cycles of switching, unlike the continuous application of linearly varying bias voltage; the obtained resistive state persists for a duration of at least 60 h. The obtained results are very important for a deeper understanding of the mechanism of resistive switching and charge transport in TiO$_2$ films, and future applications as switching material in resistance change memory based devices.

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