Resistive Switchings in Transition Metal Oxides

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0.1 Introduction.

Promising candidates for the next-generation memory devices have emerged one after another for the last decade. Ferroelectric random access memories (FeRAM), magnetoresistive random access memories (MRAM), phase change memories (PCM) are indeed at the dawn of the international development races. Along with those three fascinating memories, we focus here on probably the most seminal candidate of the future device — resistive random access memory (RRAM® or ReRAM). ReRAM consists of a simple metal/oxide/metal sandwich structure as shown schematically in Fig. 1 with myriad combinations of the metals and oxides. The sandwich shows reversible and non-volatile changes of the electric resistance by applications of ordinary electric pulses (see the right panel of Fig. 1). This phenomenon is called “resistance change” or “resistive switching”. Because of the

Figure 1 Schematic diagram of a ReRAM memory cell with a metal/oxide/metal sandwich structure and resistive switching characteristics in a Ti/Sm$_{0.7}$Ca$_{0.3}$MnO$_3$/SrRuO$_3$ cell at room temperature. By applying pulsed voltages of ±5 V, the resistance of the cell changes reversibly between high and low resistance states. (Adapted with permission from [40] ©2008 Elsevier.)
nondescript structure and simple switching operation, ReRAM is believed to hold potentially much better cell-size scalability than those of the established memory technologies even including the brand-new FeRAM, MRAM, and PCM.

It is interesting to mention that the phrase of “resistive switching” for ReRAM was taken, in literature, in a very restricted meaning, representing a sort of phenomena without a phase change, magnetoresistance, or ferroelectricity. Furthermore, this classic “resistive switching” has been praised as a precocious talent for half a century since it was discovered. The typical examples of the classic “resistive switching” were Al$_2$O$_3$-based and SiO$_2$-based sandwiches upon “electroforming” [1, 2]. Then, what is the electroforming? In short, it is an application of a voltage above a certain critical value to the sandwich to draw out the latent resistive-switching properties [3, 4, 5, 6, 7]. This electroforming or simply forming was believed to be an inevitable process for the “resistive switching”; we will classify several types of electroformings in the following, and suggest the necessity of the process.

Extensive reviews of the classic “resistive switching” had been already given around 1970s and 1980s by Dearnaley et al. [8], Biederman [9], Oxley [1], and Pagnia et al. [10]. Those reviews successfully identified the key players: voids, dislocations, and defects, which are, in a word, nonstoichiometry unavoidable in every oxide thin film. Nevertheless, around the middle of 1980s, the research on this topic was rapidly left on the backburner. This was probably because of the legendary discovery of the high-temperature superconductivity in Cu oxides in 1980s [11], toward which most of the physicists and chemists in the field of metal-oxides steered the course of their researches. Moreover, the epoch-making invention of the flash memory was also done in 1980s. This charge-storage-type nonvolatile memory gave a great impact in the field of electronic engineering. The two incidents above have balked further application research of the classic “resistive switching” phenomena.

However, since around the year of 2000, it has become highest concern that the stronghold of the charge-based memory are being imperilled due to the technical and physical limitations of miniaturisation. Then, a renewed interest of the resistive switching phenomena was resurfaced [13, 14, 15, 16, 17, 18, 19, 20, 21]. Among the new works, notably pioneering ones were done by Beck et al. [22] and Liu et al. [23] demonstrating resistive switchings in new types of perovskite transition-metal oxides. Because the former was reported by the research institute of IBM, and because the latter researchers were in collaboration with SHARP [24, 25], the two reports were widely appreciated and the prospectivity of the metal/oxide/metal sandwiches for the future nonvolatile memory was renowned. Furthermore, Seo et al. in SAMSUNG [26, 27] reported another type of resistive switching using a binary oxide NiO, which has ignited new-generation experimental works [28, 29, 30, 31, 32, 33, 34, 35] and theoretical works [36, 37, 38]. Eventually, these new works have rekindled the long-running controversy on the microscopic mechanisms behind the resistive switching phenomena.

With regards to the latest research results, the classic and rather exclusive definition of the “resistive switching” is considered to be antiquated or rather pointless. This is because the different phenomena encompassing the broad range of physics were only naively classified so far by the differences of oxides. Therefore, several re-
cent works [39, 40, 41, 42] reviewed again the smorgasbord of resistance-switching phenomena including the latest results, and have labelled not only the materials difference but also the key features from renewed points of views. The common key words are uniform or local, as well as drift or diffusion. If the resistive switching depends on the polarity of the external bias voltage, drift movement of charges (ions or vacancies) is the central character, causing the valence change at the interface. Meanwhile, if it is independent of the polarity, thermal diffusion is more essential for driving the resistive switching.

Of course, we think it may be too early to take up a unified stand. Considerable time will have been spent before the microscopic mechanism of each resistive switching phenomenon is fully understood and incontrovertible.

Our aim here is to add another unique point of view to those recent reviews in order to encourage more comprehensive researches on the resistive switching phenomena. We present a one-look overview of the resistive switching by schematically classifying their typical current-voltage ($I-V$) hystereses. For a space constraint, we especially focus on one of the classified — bipolar continuous switching, and its possible device applications.

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Classification of current-voltage hystereses

The $I-V$-hysteresis is, in general, a good measure of the electronic properties of materials and interfaces. The resistive switching phenomenon can be attributed to one of the typical hystereses shown below. However, it should be noted that many samples of resistive switching are rather complex; i.e., they are built-in serial and/or parallel connections of the resistive switching with different $I-V$-hystereses. Moreover, the $I-V$-hystereses may depend on the sweep rates of bias voltage/current, which are not specified in many experimental papers. We therefore have to preface the classification shown below is never monolithic, and its boundaries are essentially blurred. Nevertheless, we believe this kind of terse classification will be helpful for organising and reconstructing a volume of researches in this field.

Continuous and fuse-antifuse switchings.

At first view, $I-V$-curves of the resistive switching phenomena are classified into two different types as shown in Fig. 2. The top row corresponds to the so-called fuse-antifuse switching, while the bottom one is called the continuous switching. In the left panels of Fig. 2, the blue lines correspond to the low resistance state (LRS), while the red lines correspond to the high resistance state (HRS). The resistive switching from high to low resistance states is called “set”, while the opposite is called “reset”.

In general, the resistance change can be ascribed to spatiotemporal pattern formations under sufficiently high electric field or current [45, 46, 47]. When an inhomogeneity of voltage is formed, N-type negative differential resistance (NDR) is observed. Meanwhile, when a current filamentation is done, S-type NDR is ob-
erved. The example of the continuous switching shown in Fig. 2 exhibits a kind of N-type NDR manifesting the formation of the inhomogeneous electric field inside the device. In general, NDR does not guarantee the formation of the inhomogeneous electric field inside the device. We denote NDR in Fig. 2 as “NDR” to distinguish from the classic and volatile NDR. For “NDR”, the derivative is not indeed negative in several cases. It is widely believed this “NDR” is due to a non-volatile inhomogeneity formation, which is a Schottky barrier alternating its height/width continuously at the metal/oxide interface due to the drift of charged ions and defects [48, 49, 50]. Trap-detrapping of the drifting electrons may also cause the continuous switching with the “NDR”. [51, 41].

A sudden change of resistance at a “threshold” is observed in either of the $V$- or $I$-sweep measurement [52]. However, as shown in the example of the fuse-antifuse switching, the abrupt change of the resistance at the threshold (open circles in Fig. 2) can be observed both of the $V$- and $I$-sweep measurement. This is distinctly different from the conventional threshold switching and cannot be understood on an equal footing with the continuous switching. Recently it has been demonstrated that the current flows inhomogeneously through the oxide in the low-resistance state, while, in contrast, it remains rather homogeneous in the high-resistance state. [43, 62, 63] This suggests the existence of a current constricting structure, most probably at the interface. Thanks to the constriction, the current density becomes extremely large especially when the resistance state changes from low to high. A shared understanding in this research field is that the sudden change of resistance is related to the current constricting structure, which is popularly called as “filament” or, in a more specific understanding, as an electric “faucet” at the interface. The local current path is cut and connected by a local phase transition, and the switching is thus called a

![Figure 2](image_url)

**Figure 2** Schematic $I$-$V$-curves for the fuse-antifuse switching (top left) and continuous switching (bottom left). Corresponding examples [43, 44] are shown. (Reprinted with permissions from American Physical Society and Japan Society of Applied Physics, respectively.) For the fuse-antifuse switching, opaque circles denote the threshold points at which sudden resistance changes occur. The sudden changes are equally seen in both the $V$- and $I$-sweep measurements. The continuous switching exhibits a negative differential resistance (NDR), which reads as “NDR” because it is non-volatile and in many cases the derivative is not indeed negative.
fuse-antifuse type. The local phase transition, especially a metal-insulator (MI) transition, can be either structural or electronic transition, however the most important point is the locality \([5, 8, 10, 28, 30, 33, 43]\) of the current path and the transition, which makes the switching abrupt compared with the time scale of \(V\)- or \(I\)-sweep. It should be noted here that, even when a clear “filament” is formed through the oxide, the tip of the filament (faucet) at the interface with the metal electrode does not always show the fuse-antifuse action (phase transition) but sometimes shows continuous switching. This is due to the delicate balance of the drift/diffusion (strength of the current density) of vacancies and ions and the sweep rate of the applied voltage and current; this important issue is reviewed more below.

**Polarity dependence and the origin symmetry.**

In this review, we focus on the self-crossing \(I-V\)-curves passing through the origin of the \(I-V\)-plane. The resistive switching with the self-crossing \(I-V\)-curves show (topo-

![Figure 3: Classification of \(I-V\)-hystereses.](image)

**Figure 3** Classification of \(I-V\)-hystereses. Blue and red lines correspond to low and high resistance states, respectively. Arrows indicate the direction of the hystereses. Origin symmetry means the topology of the hysteresis are symmetric with respect to the origin of the \(I-V\)-plane. The patterns which cannot be drawn even schematically, those without any obvious examples, or those irreversible are shaded. Four patterns remain: (a) bipolar fuse-antifuse type due to, e.g., local redox reactions and Mott transition, (b) nonpolar fuse-antifuse type related to the thermochemical reaction, (c) bipolar continuous type due to the potential inhomogeneity by the ion/defects migration, and (d) “memristor” type, where thick black arrows indicate the characteristic behavior only seen in the “memristor” type. The (b)-type is conventionally called “unipolar” but to be exact it should be called nonpolar. See text for details.
logically) origin-symmetric high and low resistance states as schematically plotted in Fig. 3 (typical examples are seen in Fig. 4). If the switchings between the two states are dependent or independent of the polarity, the topology of the I-V-curves becomes origin-asymmetric or origin-symmetric, respectively.

An explanation of the origin-symmetry (polarity-independence) is given by assuming that the Joule heating and thermal diffusion of ions and defects could be dominant. This is reasonable because the Joule heating is independent of the polarity of applied voltage or current. (It is interesting to note here that other heatings, such as due to tunnelling-electron energy deposition is polarity dependent.) Likewise, the origin-asymmetry (polarity-dependence) can be naturally associated to the electric-field drift of ions and defects along the direction of applied voltage or current. If the diffusion of, e.g., oxygen ions is dominant, the system requires the supply of oxygens from outside, that is, from either the atmosphere or some kind of metal electrodes which work as oxygen reservoirs [55]. On the other hand, the electric-field drift of oxygen does not necessarily require the oxygen from outside; i.e., the oxygens are self-supplied or recycled by the alternating electric field [55]. In fact, by controlling the strength of electroforming, by modifying the metal/oxide interface, and by changing the atmosphere, the size/amount of the local current paths are considered to be tuned [34, 56]. Those will change the diffusion/drift balance, which alters the origin-symmetric nonpolar I-V-hysteresis into origin-asymmetric bipolar I-V-hysteresis, and vice versa.

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**Figure 4** Typical examples [43, 53, 54, 40] of the I-V-hystereses (a), (b), (c) and (d) shown schematically in Fig. 3 (Reprinted with permissions from American Physical Society, Institute of Physics, Nature Publishing Group, and Elsevier, respectively.) In practical devices, I-V-curves are given as that of serial and/or parallel connections of those I-V-curves, and each may depend on the sweep rate. Thus, the examples are not disparate and sometimes they change their types over the blurred boundaries.

The origin-asymmetric bipolar resistive switching is considered to be caused by the valence change of cations in the oxide [39, 40, 42]. This is indeed the redox reaction. In several combinations of the oxide and metal electrode, the averaged
free enthalpy of oxygen segregation is close to the free reaction enthalpy of oxide precipitation from the metal. [64] Therefore, one may conjecture that a large current density could easily drive local chemical reactions such as electro-oxidation [65, 66] and electro-reduction, [67] and the reactions may be drastically accelerated by a local Joule heating due to the strong current inhomogeneity. By considering the defects chemistry [57], the direction of the polarity (clockwise or counter-clockwise) of the bipolar switchings are well-explained. Another mechanism of the valence change is the doping-induced Mott-Hubbard transition (called simply as Mott transition), i.e., the electron-correlation-driven MI transition [37, 58, 59]. Interestingly, when the size of the system becomes smaller, the implication of the Mott transition resembles more to that of the redox reaction.

**Phase-delay response — memristor.**

Origin-symmetric bipolar $I-V$-hystereses have been reported recently [54, 60]. The unique hysteresis curve is explained as due to the history-dependent features. $I-V$-relation is expressed as $V(t) = R[q(t)]I(t)$, where $q(t) = f[I(t)]$, $t$ is time, and $f$ is an arbitrary functional of the current [61]. This $R[q(t)]$ is now known as “memristor”, which means the resistance depends on the past states (memory) through which the system has evolved. It is argued that the memristive behaviour is caused by an rearrangement of charged ions and defects under the effect of external electric field.

The mechanism is similar to that of the origin-asymmetric bipolar $I-V$-hystereses, but history-dependence is more dominant than the redox reaction. We denote here “memristor” as it is used in the original definition [60]. This original “memristor” is often confused with the (c)-type resistive switching in Fig. 3, but the apparent difference is that there are two “NDRs” in the “memristor” type hysteresis (this is sometimes called a figure-of-eight loop). One “NDR” which is indicated by the thick black arrows in Fig. 3(d) is quite unique. When the absolute value of the voltage is increased, this “NDR” does not appear, however, when the absolute value of the voltage is decreased, this “NDR” is observed. This is hardly explained by a naive redox reaction, for which the reaction occurs whenever the voltage exceeds a threshold value. However, this original and pure “memristor” type hysteresis is not very appropriate for the nonvolatile memory. For better retention, the other type of hystereses are incorporated, which makes the hysteresis of practical memristors rather similar to the origin-asymmetric bipolar types. Another possible way to fit up the non-volatility to the original “memristors” is to utilise the temperature inhomogeneity. Given that the diffusion of vacancies or ions are non-linearly accelerated by the Joule heating, then the vacancies or ions can diffuse less when the Joule heating is smaller; this is seen to be non-volatile for a scale of time, and the hysteresis is kept origin-symmetric.
Electroforming.

As described above, the resistive switching hardly occurs when the metal/oxide/metal sandwich is in the featureless initial state as schematically drawn in the left panel of Fig. 5. Initiation to enable the resistive switching is called electroforming or simply forming [3, 4, 5, 6, 7]. After the electroforming, many types of “inhomogeneity” are created in the oxides (middle panel of Fig. 5), which are manifested by the various kind of \( I-V \)-hystereses classified in Fig. 3. The variety of the inhomogeneity is caused by several factors and their combinations: some of them are the degrees of non-stoichiometry of oxides, difference of the electron affinities of oxides and metal electrodes, structural/electronic instability of oxides, as well as heat capacity/conductivity of oxides and metal electrodes [42]. The gas atmosphere, especially oxygen and moisture, is also responsible [55, 68]. With regard to the gas atmosphere, it should be noted that some kinds of oxides and metal electrodes can behave as reservoirs of those gases [55]. Joule heat generated during the electroforming provides the system with the thermal energy which is necessary for the oxides to give rise to the inhomogeneous structure. The heating is controlled by the so-called

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Figure 5 Schematic illustration of the electroforming. Blackness of the electrodes and oxides corresponds to the smallness of the resistance as indicated by the greyscale at the bottom-left corner. By the electroforming, inhomogeneity is created in the oxide bulk, and some of the structures are called “filament”. Essential structures are marked by the open squares of thick grey lines in the middle panel, i.e., faucets and interface states. The change of resistance at the faucet and interface state is responsible for the resistive switching. See text in detail.
“compliance” [69, 70] and also by the parasitic current components [71, 72]. Here the compliance current/voltage is the maximum current/voltage which can be intentionally set in order to limit the heat generation and dielectric breakdown during the electroforming.

The electroforming reduces the resistance of the sandwich if the electric bias generates a significant amount of ionic defects (e.g., oxygen vacancies and metal interstitials) in the oxides and the defects form the conducting paths [41]; meanwhile the electroforming increases the resistance of the sandwich if the defects are assembled at the metal/oxide interface rather uniformly to form a Schottky barrier [48, 49, 50]. Thus, the most essential point of the electroforming for the subsequent resistive switching is not the whole structure of the inhomogeneity but is the tiny region as is indicated by the open squares of thick grey lines in the middle panel of Fig. 5. The tiny current-constricting structure is called “faucet” due to the similarity to the tap of electric current [43], while the “interface state” (described in the following sections) denotes the voltage drop region at the interface [40]. As schematically shown in the right panel of Fig. 5, if the fuse-antifuse-type changes of resistance (i.e., local metal-insulator transition) is occurred in the tiny region, the resistance switching becomes either (a)- or (b)-type of Fig. 3. On the other hand, if the continuous movement of ionic defects are dominant in the tiny region, the resistance switching becomes either (c)- or (d)-type of Fig. 3. Therefore, it should be noticed that, even in the presence of clear filament structures in the oxide, the resistance switching can become the memristor-type or the bipolar-continuous-type switching.

From the application point of view, eliminating the electroforming process is an important and an inevitable problem. There are several reasons: large power consumption and instability of the electroforming process, as well as the accompanied gas release, which may induce physical damages on several semiconductor devices on the same chip. The schematics in Fig. 5 tell us that an approach to engineer a ReRAM device without electroforming is to eliminate the unnecessary filament and bulk regions while leaving the essential faucets and interface-state regions. For that purpose, a natural approach is to thin the oxide or make the size of the device as small as that of a faucet [73]. There have been several reports along with this approach suggesting indeed the electroforming-free ReRAM, however, these devices tend to be degraded rapidly with the switching cycles probably due to the lack of a reservoir for the mobile ionic defects. A breakthrough idea on this issue is eagerly anticipated.

As above, we have categorised the resistance switching into four types: (a)–(d) in Fig. 3. Each of them has strengths and limitations, which are all interesting to be reviewed here. However, because of the limitation of our ability and the spaces, we refrain from discussing each example in detail. Instead, in the following, we focus on a possible mechanism of (c)-type resistive switching, i.e., “bipolar continuous switching” and in brief its possibility for applications.
Bipolar continuous switching

In this part, semiconducting perovskite oxides Pr$_{1-x}$Ca$_x$MnO$_3$ (PCMO) and Nb-doped SrTiO$_3$ are brought into focus as model materials of the bipolar continuous switching [(c)-type resistive switching in the classification of Fig. 3].

Continuous switching at interface

As discussed above, the resistive switchings can be classified into two types in terms of the uniformity of the current path: one is the fuse-antifuse switching and the other is the continuous switching. They are further classified into origin-symmetric and origin-asymmetric switching depending on the balance of drift/diffusion of charge migration and that of temperature/potential inhomogeneity.

The (c)-type continuous resistive switching is caused by the drift of ions or charged vacancies under uniform electric current and inhomogeneity of the electric field. The uniform electric current is evidenced by the area dependence of the junction resistance; the junction resistance is inversely proportional to the junction area, indicating that switching takes place over the whole area of the junction, *i.e.*, the entire interface [74]. Therefore, this resistive switching is often referred as “homogeneous.

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\text{Figure 6} \quad I-V \text{ curves for (a) p-type } M/\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3/\text{SrRuO}_3 (M/PCMO/SRO) \text{ with } x = 0.3 \text{ and (b) n-type } M/\text{SrTi}_{0.99}\text{Nb}_{0.01}\text{O}_3/\text{Ag} (M/\text{Nb:STO}/\text{Ag}) \text{ cells } (M = \text{Ti, Au, and SRO}). \text{ Current rectification with hysteresis is seen in the } I-V \text{ curves for the Ti/PCMO/SRO cell, and that with opposite polarity is seen in Au/Nb:STO/Ag and SRO/Nb:STO/Ag cells. (Reprint with permission from [40] ©2008 Elsevier.)}
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interfacial resistive switching”.

In the bipolar continuous switching, the switching characteristics generally depend on the electrode materials [49, 75, 40]. Figure 6 shows I-V curves for \( M/Pr_{1-x}Ca_xMnO_3/SrRuO_3 \) (\( M/PCMO/SRO \)) with \( x = 0.3 \) and \( M/SrTi_{0.99}Nb_{0.01}O_3/Ag \) (\( M/Nb:STO/Ag \)) devices, where PCMO and STO are p- and n-type semiconductors that are the most popular materials for bipolar continuous switching [40]. \( M = \text{Ti, Au, or SRO} \) is the top electrode with the work function of \( \approx 4.3, \approx 5.1, \) and \( \approx 5.3 \) eV, respectively. The SRO and Ag are bottom electrodes, which form ohmic contacts with PCMO and Nb:STO, respectively. For the p-type PCMO cells, as the work function of \( M \) decreases, the contact resistance between \( M \) and PCMO increases, and the Ti/PCMO interface shows rectification behaviour in the I-V curves. On the other hand, for the n-type Nb:STO cells, as the work function of \( M \) increases, the contact resistance between \( M \) and Nb:STO increases, and the Au/Nb:STO and SRO/Nb:STO interfaces show rectification behaviour in the I-V curves.

The rectification of current is due to a Schottky-like barrier at the interface, as shown in the insets of the lower panels of Fig. 6. In addition to the rectification, I-V curves for Ti/PCMO, Au/PCMO, and SRO/Nb:STO interfaces exhibit hystereses indicative of resistive switchings. However, the ohmic I-V curves for Au/PCMO, SRO/PCMO, and Ti/Nb:STO interfaces show no resistive switching. These results suggest that the Schottky-like barrier plays a key role of the (c)-type resistive switching. Since this is a bipolar valence change switching, the polarity of the applied bias relative to the Schottky bias is important. The resistance changes from HRS to LRS only when a forward bias voltage is applied to the interface, and it changes from LRS to HRS only when a reverse bias voltage is applied, as shown in the lower panels of Fig. 6.

Valence change of transition-metal cations

As mentioned above, the bipolar continuous switching is considered to be caused by the valence change of cations in oxides. In such a case, the valence of cations may be a crucial parameter for controlling the resistive switching characteristics. In fact, it has been reported that the resistive switching characteristics of the Ti/PCMO devices depend on the Mn valence [76]. Figure 7 shows the Ca-composition, \( x \), dependence of resistive switching ratios, \( R_H/R_L \), for the Ti/Pr\(_{1-x}\)Ca\(_x\)MnO\(_3\) devices, where \( R_H \) and \( R_L \) are resistances of high- and low-resistance states, respectively. Assuming no oxygen vacancy in the Pr\(_{1-x}\)Ca\(_x\)MnO\(_3\) layer, the Mn valence increases from 3+ to 4+, as the Ca-composition \( x \) increases from 0 to 1, respectively. The resistive switching ratio \( R_H/R_L \) increases with increasing \( x \) and shows a maximum value at around \( x = 0.4 \). As \( x \) increases above 0.4, \( R_H/R_L \) decreases and becomes smaller than 2 for \( x > 0.8 \). This clear \( x \) dependence of \( R_H/R_L \) evidences the importance of the valence of cations for the bipolar continuous switching.

In the resistive-switching process, the oxygen-vacancy density at the interface between a metal electrode and oxide is changed due to the electric-field-induced drift of oxygen vacancies or ions. As a result, the change in the oxygen-vacancy density causes the valence change of cations at the interface. This can be confirmed...
Figure 7 Ca-composition, $x$, dependence of resistive switching ratio $R_{H}/R_{L}$ of Ti/$\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ junctions measured at room temperature. $R_{H}/R_{L}$ clearly depends on $x$, indicating that the Mn valence is a crucial parameter for controlling the resistive switching characteristics.

by a cross-sectional transmission electron microscope (TEM) measurement with an electron energy loss spectroscopy (EELS) [44, 76]. Figure 8 shows cross-sectional TEM images of the Ti/PCMO junctions with $x = 0.5$ [76]. At the cross-section of the as-prepared junction of a Ti electrode and a PCMO layer (before applying electric field), there was an amorphous TiO$_y$ (a-TiO$_y$) layer with a thickness of at most 1 nm. After applying electric fields above 5 V, the thickness of the a-TiO$_y$ layer was increased to $\sim 10$ nm, as seen in Fig. 8(b). The formation of a-TiO$_y$ layer indicates an electromigration that oxygen ions are drifted from the PCMO layer into the Ti electrode. Moreover, EELS measurements of the Mn-$L$ edge confirmed the valence

Figure 8 Cross-sectional TEM images of a Ti/PCMO junction observed (a) before and (b) after applying electric field at room temperature. Before the field application, a thin amorphous TiO$_y$ layer ($< 1$ nm) was confirmed between the Ti and PCMO layers. After the application of voltage stress, the thickness of the amorphous TiO$_y$ layer was increased to $\sim 10$ nm. (c) Mn-$L$ edge EELS spectra at several positions around the Ti/PCMO junction. The positions are indicated in (b). Each spectrum was normalised by the intensity of the Mn-$L_2$ peak. (Adapted with permission from [76] ©2009 APS.)
change of the Mn site. Figure 8(c) shows the Mn-$L$ edge EELS spectra obtained at different positions in the PCMO layer, as indicated in Fig. 8(b). The peak intensity ratio of Mn-$L_3$ and Mn-$L_2$, $I(L_3)/I(L_2)$, was decreased with increasing the distance from the a-TiO$_y$/PCMO boundary. This means the Mn valency near the interface is smaller than that away from the interface.

**Alteration of the barrier characteristics**

Electric field drift of the oxygen ions and oxygen deficiencies cause the valence change of the transition metal as well as the lattice disorders, both of which lead to the change in the electronic states of the transition metal oxides. Figure 9 shows optical absorption spectra of oxygen-deficient and oxygenated PCMO films [76]. The oxygen-deficient PCMO film has a larger absorption gap compared with that of the oxygenated one. In a Mn-O-Mn chain in PCMO, the lack of the oxygen suppresses the overlap of the neighbouring Mn $e_g$ orbitals. Then, the effective $e_g$ band width is reduced and the optical absorption gap is increased [77, 78].

The TEM and EELS experiments (Fig. 8) indicate that the electromigration of oxygen vacancies generates the oxygen-deficient PCMO layer in the vicinity of the interface between the a-TiO$_y$ and PCMO. The $I$-$V$ curves suggests the preferable direction of the oxygen electromigration. In the Ti/PCMO junction, when a positive voltage bias was applied to the PCMO layer, the resistance state was converted from the HRS to the LRS, as shown in Fig. 6. In this case, positively-charged oxygen vacancies are expected to drift from the PCMO layer into the a-TiO$_y$ layer. During the switching from the LRS to the HRS, oxygen vacancies are expected to drift back.

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*Figure 9* Optical absorption spectra of oxygen-deficient (blue line) and oxygenated (red line) PCMO films on STO substrates measured at room temperature. The broken straight lines are fits to the rising part of the absorption spectra, and the optical absorption gap was estimated from the intersection of the broken line at the optical absorption coefficient $\alpha = 0$. (Adapted with permission from [76] ©2009 APS.)
Figure 10 C-V curves under reverse bias for a Ti/PCMO\((x=0.3)/\text{SRO}\) device. The hysteretic characteristic indicates that the barrier width \((W_d)\) at the Ti/PCMO interface is altered by applying an electric field. The insets show possible band diagrams of Ti/PCMO interface (a) in a low-resistance state (LRS) and (b) in a high-resistance state (HRS). The work function of Ti is \(4.3\) eV, that of p-type PCMO for \(x<0.5\) is \(4.4-4.8\) eV, and the band gap of \(0.2-0.6\) eV. Therefore, a Schottky-like barrier can be formed at the interface. In the HRS, since the oxygen-deficient PCMO layer at the interface has a larger band gap, the hole-carrier conduction is interfered. (Adapted with permission from [79] ©2005 SPIE.)

to the PCMO layer from the a-TiO\(_x\) layer. Therefore, the number of oxygen vacancies in PCMO near the interface is larger in HRS than in LRS. In HRS, the highly oxygen-deficient PCMO layer has a narrower \(\epsilon_d\) band, leading to a larger band gap. This could act as an effective barrier for the hole-carrier conduction as schematically drawn in Fig. 10. On the other hand, when the oxygen vacancies in PCMO is less, the band gap is smaller. Then, the hole carriers could flow through a thin depletion layer via a tunnelling process. This is LRS as depicted in Fig. 10. The change of the barrier at the interface may alternate the hole-carrier conduction from the tunnelling to the thermionic emission. This barrier width change was confirmed by a capacitance \((C)\) measurement [79]. The value of \(C\) is given by \(C = \frac{\varepsilon_{\text{TiO}_x}\varepsilon_{\text{PCMO}}S}{(\varepsilon_{\text{PCMO}}W_a + \varepsilon_{\text{TiO}_x}W_d)}\), where \(\varepsilon_{\text{TiO}_x}\) and \(\varepsilon_{\text{PCMO}}\) are the dielectric constant of a-TiO\(_x\) and PCMO layers, respectively. \(S\) is the cell area, \(W_a\) is the thickness of the a-TiO\(_x\) layer, and \(W_d\) is the depletion layer width in the PCMO layer. The effective barrier width \(W\) is \(W = W_a + W_d\). Assuming that \(\varepsilon_{\text{TiO}_x}, \varepsilon_{\text{PCMO}},\) and \(W_a\) do not change, the change in \(C\) is attributable to the alteration of \(W_d\). As seen in Fig. 10, the \(C-V\) curve for the Ti/PCMO shows hysteretic behaviour, \(i.e.,\) the capacitive switching, and the value of \(C\) in the LRS is larger than that in the HRS. This suggests that \(W_d\) in the LRS is narrower than that
in the HRS, consistent with the possible band diagram of Ti/PCMO interface in HRS and LRS, as schematically shown in Fig. 10.

0.4 Towards device applications and summary

Due to the continued advances in information technology, there is always an ever-growing requirement for nonvolatile memory devices with faster (less than a few nanoseconds) bitwise access and with smaller cell size (less than 20 nm) for storing one bit. Practically, the emerging nonvolatile memories are to be compared with a state-of-the-art memories such as the flash memory and DRAM. A typical charge-storage-type memory DRAM is currently in the 30 nm range with a cell size of $6f^2$, where $F$ is the minimum feature size on a given process. Because it requires a three-dimensional structure of capacitors, the thickness of its dielectric limits the scalability. This is actually a chance for new types of memories to edge into, and a number of alternative nonvolatile memories of non-charge-storage types have been explored. ReRAM has attracted considerable attention, because of its simple memory-cell structure with high scalability as well as its fast switching speed [80, 39, 40].

The ReRAM memory cell has a capacitor-like structure composed of insulating or semiconducting metal oxides. Because of such a simple structure, highly scalable passive cross-point and multilevel stacking memory arrays with rows and columns of word and bit lines have been proposed [81]. For those array structures, one memory cell has an area of about $4f^2$ which is much smaller than that of DRAM. In every write/read operation, a bias voltage is applied on a memory cell through the selected word and bit lines. To ensure the reliability of the write/read operation, a selection element such as a diode or highly non-linear resistor has to be connected to a memory cell in series to prevent signal from bypassing through neighbouring “ON”-state memory cells, i.e., the so-called parasitic-path problem or the sneak current problem [39, 82].

In response to the requirement, oxide p-n diodes and Schottky diodes compatible with the metal oxides of ReRAM memory cell have been proposed [27]. However, for the ReRAM of origin-symmetric fuse-antifuse type memory cell [(b)-type of Fig. 3] with sub 100 nm scaling, the forward current densities are too large to be handled by the proposed diode selectors. Thus, for the origin-symmetric fuse-antifuse type ReRAM with the passive cross-point array structure to be realised, it is essential to develop a diode selector which has a high forward current density ($> 10^6$ A/cm$^2$) and/or to suppress the reset current density ($< 1 \mu$A) [83]. On the other hand, for the bipolar continuous resistive switching, especially, “interfacial Schottky resistive switching”, the memory cell is accompanied by the self-formed Schottky barrier, which can be used as the selection element [82]. This means that the passive cross-point memory array can be realised without stacking any selection element. This is an advantage of the interfacial Schottky resistive switching memory cell over the origin-symmetric fuse-antifuse memory cell.

Another critical issue for the future development of ReRAM is the reliability, such
as data-retention and memory endurance (the number of erase and write cycles). The variation of characteristics from cell to cell as well as from chip to chip is also an important issue to be controlled. A data-retention time over 10 years can be extrapolated from the retention characteristics measured at high temperatures [74, 84, 85], and the memory endurance over $10^{11}$ cycles has been demonstrated for the $\text{Ta}_2\text{O}_5/\text{TaO}_2$ memory cell [86]. These reported characteristics seem to be enough for an alternative to the flash memory. However, little has been investigated on the characteristic variation. A method to realise the device characteristics uniform over a large area, and an elucidation of the fatigue mechanism, are immediately worked out satisfactory for the future development of large-capacity ReRAM.

In summary, we provided a one-looking review of the recent understandings of the resistive switchings by classifying their $I-V$-characteristics. They were roughly classified into fuse-antifuse type and continuous type depending on the locality of the switching in space and time compared with the scale of device and bias sweeping time. Each of them was further classified into origin-symmetric and origin-asymmetric types, depending on the dominance of electric-field drift (potential inhomogeneity) or thermal diffusion (temperature inhomogeneity). For each category, a representative example was shown; especially, the continuous bipolar switching with alternating Schottky barrier was discussed in detail. A possible device structure when applied in a practical electronic device was introduced with regards to the ultimate scalability of the ReRAM device. We hope this concise review will help readers to understand these seemingly complicated phenomena, and will contribute to light a direction toward a viable development of new memory devices.

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