J Electroceram (2008) 21:61–66
DOI 10.1007/s10832-007-9081-y

Current status of resistive nonvolatile memories

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Published online: 4 May 2007
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Abstract Several emerging nonvolatile memories (NVMs) such as ferroelectric memory, magnetoresistive rams and ovonic universal memory are being developed for possible applications. Resistive random access memory (RRAM) is another interesting competitor in the class of NVMs. The RRAM is based on a large change in electrical resistance when the memory film is exposed to voltage or current pulses, and can keep high or low resistance states without any power. The ideal RRAM should have the superior properties of reversible switching, long retention time, multilevel switching, simple structure, small size, and low operating voltage. Perovskite oxides, transition metal oxides, and molecular materials were found to have resistive memory properties. This presentation reviews the ongoing research and development activities on future resistance NVMs technologies incorporating these new memory materials. The possible basic mechanisms for their bistable resistance switching are described. The effect of processing, composition, and structure on the properties of resistive memory materials and consequently the devices are discussed.

Keywords Nonvolatile memories · Resistance random access memory (RRAM) · Perovskite oxides · Transition metal oxides · Molecular materials

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1 Introduction

Nonvolatile memories have been extensively applied in the recent years, due to the onset of popular applications of mobile equipments. Flash memory, for example, is the main stream of the nonvolatile memory and can be found everywhere in our daily life. However, flash memory has some drawbacks such as high operation voltage and low operation speed that do not satisfy the requirements for a perfect nonvolatile memory. Therefore, several novel types of nonvolatile memories like ferroelectric random access memory (FeRAM), magnetic random access memory (MRAM), ovonic universal memory (OUM), and resistive random access memory (RRAM) are being investigated [1]. Among these nonvolatile memories, RRAM plays an important role because of its non-destructive readout, low operation voltage, high operation speed, long retention time, and simple structure.

An RRAM device consists of one resistor and one corresponding transistor or diode. The resistor, fabricated in the back-end process, is in the structure of metal/insulator/metal (MIM) with the property of tunable resistance for storage. The emerging material groups used in RRAM applications can be divided into several categories; such as perovskite oxide materials, transition metal oxide materials, and molecular materials, which are going to be discussed in this article.

2 Perovskite oxides for RRAM applications

In the recent years, perovskite structure materials such as $Pr_{1-x}Ca_xMnO_3$ (PCMO), $La_{1-x}Ca_xMnO_3$ (LCMO), LPCMO, $Pb(Zr_{1-x}Ti_xO_3)$ (PZT), $LiNbO_3$ (LNO), $SrTiO_3$ (STO), and $SrZrO_3$ (SZO) have attracted much of the

attention for their applications in nonvolatile memory. It is the property of electric pulse induced resistance (EPIR) change in the perovskite oxide where the current researchers have devoted themselves [2].

2.1 STO and SZO

Among various perovskite materials, Cr-doped $SrZrO_3$ is the most promising candidate for nonvolatile memory usage. It seems to have superior retention, larger on–off ratio, higher resistance transition speed, and lower operating voltage than other perovskite materials [1]. The typical current–voltage curve demonstrates that by applying a negative voltage, the device switches from initial high resistance state to low resistance so that the conducting current jumps form low to high. Applying a positive voltage reverts back to high resistance state, which leads to low conducting current. The sweeping voltage leads to a counterclockwise loop in current–voltage curve as shown in Fig. 1. Here, the H-state means the high conducting state, and the L-state means the low conducting state.

Beck et al. [3] proposed that the conducting mechanism in Cr-doped $SrZrO_3$ is caused by some defects that are created by dopants having different oxidation states and vacancies forming a series of states at various levels within the energy gap where the charge-transfer occurs via these acceptor and donor levels (Cr^{3+} and Cr^{4+}), and the conducting current in both states is dominated by the same mechanism where the activation energy of low and high conducting states are 30 and 10 meV, respectively. Rossel et al. [4] introduced electron-beam-induced current method to investigate the electrical transition properties indicating that the electrical switching correlates to the locally individual conducting paths composed of the intrinsic defects in the thin film.

In our Cr-doped SZO films, the high resistance state has a tendency to go to low resistance state during the dynamic voltage pulsing cycles as shown in the Fig. 2. It is apparent in Fig. 2 that there are occasionally some “soft errors” during the dynamic voltage pulsing cycles with middle resistance values between high and low resistance states, where the “soft errors” may lead to the wrongly stored-data. Such “soft errors” are believed to be one of main issues to be solved for practical applications. For some materials, the initial resistance value of the fresh device, called the original state, is different from the followed high and low resistance states before applying any voltage pulse to the switch to different states. A forming process is needed to start the switching in the device. The conduction of the L-state is satisfied by the Frenkel–Poole emission and that of the H-state follows ohmic mechanism [1]. We find that at 150 °C for 1.5 h, both L-state and H-state current decrease to retain a close value to the original state.

2.2 Colossal magnetoresistance materials: PCMO, LCMO

As for PCMO, there are two main resistance switching mechanisms recently proposed. One mechanism focuses on the interfacial layer [5–8] but the other emphasizes the effect of PCMO bulk [2, 9]. Baikalov et al. [5] argued that the reversible polarity-dependent resistance switching takes place at the Ag-$Pr_{0.7}Ca_{0.3}MnO_3$ interface possibly via an electrochemical process. Later, Tsui et al. [6] have observed that: (a) the resistance switching is a general phenomenon in the metal-oxide interfacial layer; (b) the capacitance of the interfacial layer changes with resistance switching suggesting a change of the space-charge; (c) the carrier trapping dominates the interfacial resistance without indication of Schottky barrier, and it is proposed that a pulse-driven reversible change of the trap density is responsible for the switching about the on–off resistance ratio of about 5–100; (d) according to the temperature dependency, the carrier transport property of the interfacial layer is the same in both high and low resistance states, which is different from that of the bulk. Moreover, at approximately 0.1 V, it suggests that the thermionic emission-limited conduction is the major mechanism, while the carrier injection plays a minor one; however, above 0.5 V, the space-charge limited current is suggested to be the dominant mechanism. In both conducting regions, it is worthwhile to note that the resistance ratio is roughly independent of voltage. However, Odagawa et al. [8] proposed that it is probable that the Schottky-like barriers within the depletion layer are formed at either or both of the interfaces via a carrier trapping and detrapping of the sites. Sawa et al. [7] obtained similar explanation that pulsed voltage induced resistance change occurs at the Ti/PCMO interface where trapping states have enough density to form a Schottky barrier.

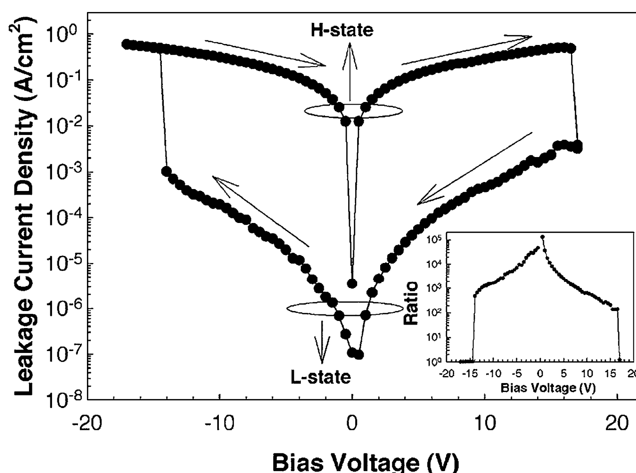

Fig. 1 I–V curve in the voltage sweeping mode for Cr-doped SZO-based MIM device. The inset shows the variation of the resistance ratio according to the bias voltage [1]

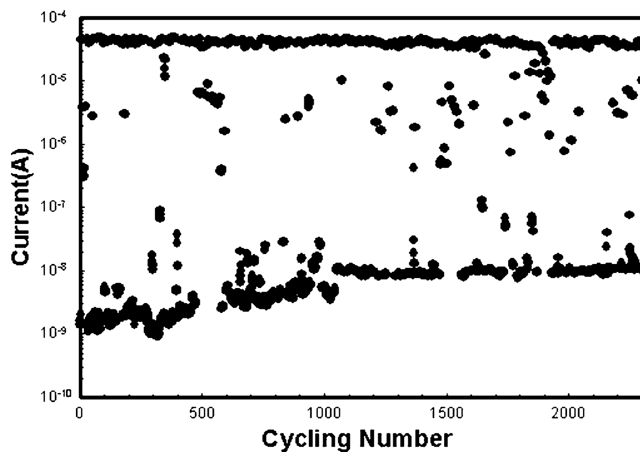

Fig. 2 Some "soft errors" occurred during the dynamic voltage pulsing cycles, which indicates middle resistance values between high and low resistance states

In conflict with the interface dominant resistance switching, Liu et al. [2] and Papagianni et al. [9] suggested that the filamentary high conductivity paths are responsible for the resistance switching mechanism of the PCOM thin film. Duhalde et al. [10] also proposed that the filamentary paths enhance the conductivity in the LCMO thin film. In respect of the fatigue behavior and the retention within Ag-LCMO-Pt system, Dong et al. [11, 12] demonstrated that the retention property depends on both the resistance states, where the metastable state is easily under fatigue, the retention could be improved by post-annealing in O_2 or be properly modified by means of tuning applied voltage pulses. It may be thought that the retention and fatigue (or called endurance) behaviors are caused by the traditional "domain wall pinning" or "hetero-charging" effect. The high resistance state has a tendency to move to low resistance state during the dynamic voltage pulsing cycles in Ag-LCMO-Pt system, and the same tendency exists in Cr-doped SZO films. However, in PCMO films, it is interesting to find out the fatigue phenomenon that finally saturates with a low resistance ratio as dynamic voltage pulsing cycles increase [2]. The fatigue phenomenon gives rise to the decaying on-to-off resistance ratio, and reduces the performance and the lifetime of the memory device.

3 Transition metal oxide for RRAM applications

In the early stage, the researches of transition metal oxide such as NiO, TiO_2, HfO_2, ZrO_2, and Nb_2O_5 mainly focused on their high dielectric constant gate oxide application, but it gradually becomes the current issue because of their good electrical properties that are required to reach the requirements of nonvolatile memory [13–16].

Baek et al. [13] studied several TMO device properties that indicate: (a) The resistance switching is independent of bias polarity. (b) The forming voltage depends linearly on film thickness. (c) Under the condition of the increasing cell size, the resistance of fresh cells decreases proportionally, while low and high resistance states slightly decrease. The threshold voltages do not change with cell size variation. (d) The asymmetric resistance transition speeds are represented, where the high resistance state transits to low resistance state at a faster rate than the low resistance state transits back. (e) The TMO devices have excellent thermal stability. Moreover, the failing devices are due to soft failure and an annealing process could effectively reduce the number of early failing ones. They argued that the low resistance state is due to the empty metallic states in the conducting filament, and these states become filled due to the injected charges by increasing bias voltage causing high resistance where the current is mainly due to the correlated barrier hopping of small polaron.

Seo et al. [14, 15] have studied that the effect of the non-stoichiometric ratio between the transition metal and oxygen on the switching properties of NiO. It was found that the more the oxygen content is in the forming gas, the more the nickel vacancies that are generated leading to an increase in the current at the high resistance state. The bistable memory switching exists in the condition of high concentration of metallic nickel defects. It was demonstrated in their advanced experiment that in the series structure, the device with higher resistance in off state is easy to induce the formation and rupture of a conducting filament in the NiO matrix. Fig. 3 shows the typical I–V curve for the resistance switching of the TMO-based device. Furthermore, there are some electrical characteristics of PCMO, Cr-doped SZO and TMO listed in the Table 1.

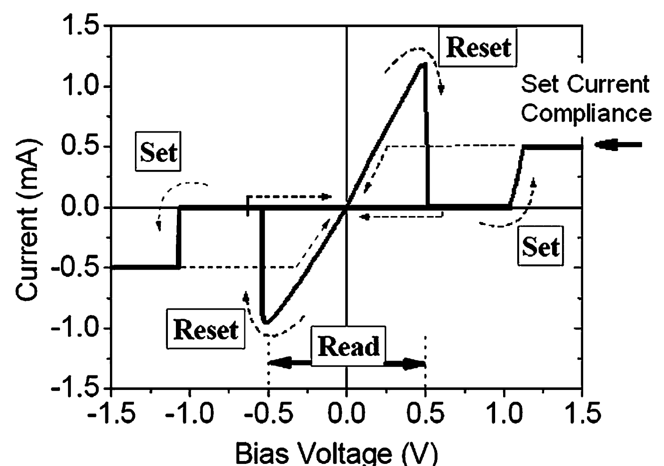

Fig. 3 Typical I–V curve for the resistance switching behavior of the TMO based device [13]

Table 1 Resistance switching behaviors of some ceramic materials.

Material	PCMO	Cr-doped SZO	TMO
Operation mode	+V turns to low resistance state −V turns to high resistance state	+V turns to high resistance state −V turns to low resistance state	Independent of bias polarity
Asymmetric transition speed	Transition from high resistance state to low resistance state is faster		
Multi-level switching	Exist	Exist	Exist
Reference	[17]	[1]	[13, 14]

4 Molecular materials for RRAM applications

In comparison to perovskite oxides and transition metal oxides, molecular memory layers are superior in the advantage of their properties that can be tailored by a selective change of the molecular structures. Besides, molecular materials are often not only suitable for vacuum deposition but also for spin-coating process to reduce process complexity. The main issues of molecular materials for RRAM are their thermal stability and reproduction. According to the resistance switching mechanisms, these materials can be divided into four groups, which are described as in the followings.

4.1 Formation of conducting filaments

Under some critical electric field, the formation or dissolution of the conducting filaments of the organic materials between two electrodes are induced to connect the two electrodes leading to drastic conductance change. Such conducting filaments may consist of (1) carbonated chains confirmed by a chromatography analysis method [18]; (2) inclusion of metal nanoparticles in organic matrix [19]; (3) metal atoms extracted from the electrode, which needs ≧60% concentration of metal atoms in the organic matrix [20].

Moreover, the conducting filaments are usually in nanoscale that sometimes may induce dot formation on the surface. Therefore, the formation of conducting filaments could be observed by means of scanning electron microscope or by atomic force microscope to measure the conductance of the switching region.

4.2 Electroreduction and oxidation of the molecules

Molecule may contain some of functional groups, like acceptor groups, donor groups, redox active groups, hydrophilic groups, or hydrophobic groups, which lead to different electrical and physical properties. It is one of the merits of molecular that we can tune the electrical properties by tailoring or attaching some functional groups by means of synthesis.

For the switching mechanism of the molecular resistive random access memory, there often exist functional groups in molecular devices if the appearance of a high conducting state is due to the electroreduction to a stable species [21]. The molecule is initially an electrical insulator. When a negative voltage that is above the reduction potential is applied, the molecule accepts an electron to reduce the accepter groups resulting in redistribution of electrons in the benzene rings(if the molecule had) leading to overlapping of electronic structure that changes to a high conducting state. On the other hand, when returning to low conducting state, there is a positive voltage that is applied in order to oxidize by means of removing the electrons that are previously accepted. Moreover, it is interesting that the molecules with donor and acceptor groups have higher leakage current in low conducting state due to the electrons from donor groups lower the barrier heights [21]. Therefore, the electron acceptor groups are often of critical importance for the conductance switching.

4.3 Interfacial effects dominating the conductance change

The electrical conductance change of the sandwich structure (top electrode/molecule/bottom electrode) could be

Table 2 List of some good resistance switching properties reported.

Material	PCMO	TMO	Cr-doped SZO	Molecular
Switching voltage (V)	5	3	15	3.8
Resistance ratio	10~1,000	10~1,000	10^3~10^5	>100
Temperature stability (°C)	>200	250	250	300
Endurance cycles	~10^3	>10^6	10^3	10^6
Retention	1,600 min at 85 °C	>8 months	1,800 s at 85 °C	>8 months
Reference	[9, 17]	[13]	[1]	[34]

influenced by the interface between the top electrode and molecular films, or that between molecular films and bottom electrode, or both. Kshida et al. [22] speculated that the conductance switching phenomenon is due to the difference in the interface between the top electrode and the molecular films under various conditions of top electrode. This process decides whether it exhibits conductance change or not and, moreover, the voltage that is required for conductance switching is independent of the number of the middle molecular layers. Besides, it has been reported that three different molecules were used in the Pt/monolayer/Ti device structure and each of them has similar hysteretic behavior and the resistance even could be continuously tuned between two extremes of high and low state [23]. More articles ascribe the switching behavior to the effects of the interfacial space charges [24].

It is usual to see that the conductance switching arising due to the interfacial effects leads to less reliability in the properties compared to those due to other mechanisms.

4.4 Charge trapping or inclusion doping induced conductance switching

It has been reported in the past several years that there are various conductance switching phenomena, especially, in multilayer structures, which are relative to charge trapping or inclusion doping. As mentioned in the well-developed semiconductor materials, doping plays an important role in the significant change of the conductivity, and it is likely to modify the molecular films by the same way. The nonvolatile electrical bistability of the tri-layer structure between the top and the bottom electrodes has been reported recently [25]. The tri-layer structure is composed of a metal layer embedded in the middle of two organic films. It is suspected that the trapped charges of the embedded metal layer and the dynamic doping process of organic films are responsible for the conductance switching effect, and there is no switching phenomenon in just one organic layer between both electrodes. Based on the result of their further investigations, it is shown that the nanocluster of the middle metal layer dominates the switching phenomenon.

Under low deposition rate of the middle metal layer, the charge-storage of partially oxidized nanoclusters is characterized by AFM, the UV-visible absorption, and in situ X-ray photoemission spectroscopy. As the device is in the high conductance state, the nanoclusters trap the charges and are polarized leading to larger capacitance than that in the low conductance state. It is believed that the charge storage at the embedded metal nanocluster layer subsequently induces charge at the organic layers, similar to the doping process in organic materials, leading to the conductance switching phenomenon. Latter, Kang et al. [26] demonstrated that the organic device with a charge trap layer, which is very thin (usually <10 nm) to get discrete and cluster metal islands, shows conductance switching behavior.

The phenomenon of negative differential resistance (NDR) is usually observed in the current–voltage curve of a molecular electronic device if its conductance switching is mainly by means of charge trapping [25]. Therefore, it may be a way to discuss and judge the possible switching mechanism in advance.

Although various possible mechanisms have already been reported in the articles, such as conformational changes [27], bond fluctuation between the molecules and their contacts [28], rotation of functional groups [29], metallization and de-metallization of metal ion diffusion in the organic film [30], isomerization reaction of photochromic diarylethene molecule via its excited state by electric carrier injection [31], molecular reorienatation [32], and dissociation of ionic complex of one-dimensional molecular system [33], it still needs further works to find out the dominant mechanism for the switching behavior. Because there are several kinds of molecules having bistable states with different conductance, it is obvious that their dominant mechanism has to be identified to explain both the high and the low conducting state and how it changes the conductance reversibly.

5 Conclusions

There are various possible mechanisms existed to explain the switching behaviors of various ceramic and polymer materials including PCMO, Cr-doped SZO, TMO, and some kinds of molecular materials. These materials seem to have good potential for the NVM applications. But it needs a lot of efforts to obtain better understanding on the relationship between the inner physical and chemical changes of the materials and drastic resistance change while applied voltage pulse or current pulse, in order to be able to produce more reproducible and reliable RRAM for practical applications. Some good resistance switching properties reported in the literature are listed in Table 2.

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