Review
Chinese Science Bulletin

Optoelectronics

April 2012 Vol.57 No.11: 1235–1240
doi: 10.1007/s11434-011-4930-0

Improving the electrical performance of resistive switching memory using doping technology

WANG Yan[1,2], LIU Qi [2], LÜ HangBing [2], LONG ShiBing[2], WANG Wei[1], LI YingTao[1,2], ZHANG Sen[2], LIAN WenTai[2], YANG JianHong[1] & LIU Ming[2*]

[1] College of Physical Science and Technology, Lanzhou University, Lanzhou 730000, China;
[2] Laboratory of Nano-Fabrication and Novel Device Integration, Institute of Microelectronics, Chinese Academy of Sciences, Beijing 100029, China

Received July 7, 2011; accepted November 21, 2011

In this paper, improvements of resistive random access memory (RRAM) using doping technology are summarized and analyzed. Based on a Cu/ZrO_2/Pt device, three doping technologies with Ti ions, Cu, and Cu nanocrystal, respectively, are adopted in the experiments. Compared to an undoped device, improvements focus on four points: eliminating the electroforming process, reducing operation voltage, improving electrical uniformity, and increasing device yield. In addition, thermal stability of the high resistance state and better retention are also achieved by the doping technology. We demonstrate that doping technology is an effective way of improving the electrical performance of RRAM.

non-volatile memory, resistive random access memory (RRAM), doping technology

Citation: Wang Y, Liu Q, LÜ H B, et al. Improving the electrical performance of resistive switching memory using doping technology. Chin Sci Bull, 2012, 57: 1235–1240, doi: 10.1007/s11434-011-4930-0

How far floating gate based memory can extend and what the further direction of next generation memory is, are two research questions that have attracted extensive attention and concern. To solve the shortcomings of conventional memories, several new emerging memories, including magnetic random access memory (MRAM), ferroelectric random access memory (FRAM), phase-change random access memory (PRAM), and resistance random access memory (RRAM), have been studied as candidates for future memories [1]. Of these candidates, RRAM devices based on binary metal oxide (BMO) have received considerable research attention because of their advantages of simple device structure, high density, excellent scalability, fast switching speed, low energy consumption, and compatibility with CMOS technology [2].

In general, RRAM has a sandwich structure of metal-insulator-metal. The “metal” here denotes a material with good electrical conductivity [3], where Cu, Ag, Pt, Ti, and TiN are the materials most frequently used as electrodes in this capacitor-like structure [4–8]. Several BMO materials such as ZrO_2 [9], HfO_2 [4,8], TiO_x [10], ZnO_2 [5], NiO [11], CeO_x [12], Ta_2O_5 [13], CuO_x [14], and WO_x [15] have been reported as the insulator layer in RRAM. Under an appropriate electric stimulus, the resistance of the insulator layer can be switched between a high resistance state (HRS) and a low resistance state (LRS). The memory effect is realized by the different resistance states. Although the mechanisms responsible for the resistive switching behaviors in different materials are still being debated intensely, the critical role of defects and impurities in resistive switching has been recognized. Unfortunately, the intrinsic defects (i.e., dislocation, grain boundary, ions, or vacancy) in BMO films are inhomogeneously and nonuniformly distributed and difficult to control. RRAM devices with pure BMO films often exhibit unfavorable memory performance, i.e., low device yield, high operation voltage, low uniformity, and poor device stability,

---

*Corresponding author (email: liuming@ime.ac.cn) which hampers their application in industry [16].

Several research groups have adopted doping technology as an effective method for solving above problems. It has been demonstrated that the performance of BMO-based RRAM devices can be greatly improved by intentionally introducing homogenous impurities in the BMO films [16–24]. In this paper, we discuss the effect of doping technology on the resistive switching characteristics of RRAM devices. Undoped Cu/ZrO_2/Pt devices are fabricated for comparison, while three types of doping technology including Ti, Cu, and Cu nanocrystal (NC) in the Cu/ZrO_2/Pt are referred to in our discussion.

Ti impurities are doped in the ZrO_2 films using the ion implantation method, while the Cu and Cu NC impurities are introduced using a thermal diffusion method. The detailed fabrication processes of the Cu/ZrO_2:Ti/Pt, Cu/ZrO_2:Cu/Pt, and Cu/ZrO_2:Cu NC/Pt devices have been described, respectively, in our previous papers [17,23,24]. The control samples (Cu/ZrO_2/Pt) without doping impurities are simultaneously fabricated to investigate the impact of doping impurities on the resistive switching behavior. The electrical parameters for these devices are measured with the Keithley 4200 semiconductor characterization system and Agilent 81110A pulse pattern generator. For the electrical measurements, the bias polarity is defined with reference to the bottom Pt electrode.

1 Characteristics of undoped-BMO-based RRAM devices

Figure 1 shows 10 cycles of the current-voltage (*I-V*) curves of the Cu/ZrO_2/Pt device under DC voltage sweep. As can be seen from this figure, the resistive switching characteristics of the undoped RRAM device exhibit two weaknesses. (i) An electroforming process with a high voltage (~10 V) is needed to trigger resistive switching behaviors. In this process, a 1 mA current compliance is used to prevent the BMO films from hard breakdown. (ii) A wide distribution of the resistive switching parameter is shown in the undoped RRAM devices. The V_{Set} and V_{Reset} are, respectively, the threshold voltages from the HRS to the LRS, and vice versa. For the undoped Cu/ZrO_2/Pt device, the distributions of V_{Set} and R_{HRS} have wide ranges. A high electroforming voltage and poor electrical uniformity are also observed in other undoped-BMO-based RRAM devices, such as TiN/HfO_2/Pt, Pt/TiO_2/Pt, and Pt/NiO/Pt [25–27].

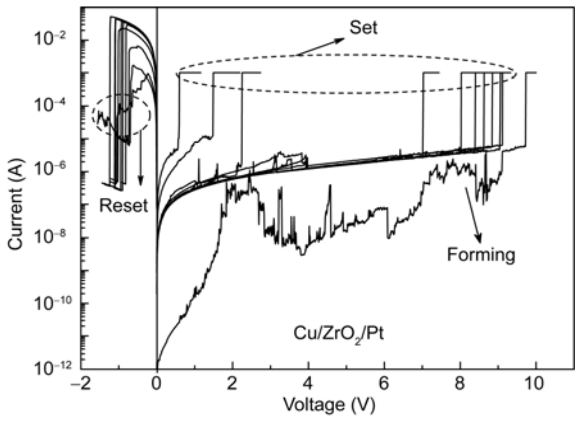

Figure 1 Reproducibility of the resistive switching (10 cycles) of the Cu/ZrO_2/Pt device under DC voltage sweep. Here, the cell size is 100 μm × 100 μm and the ZrO_2 thickness is 70 nm.

Additionally, low device yield is also observed in the undoped-BMO-based RRAM devices. For example, only about 40% of the cells of the Cu/ZrO_2/Pt devices show the repetitive resistive switching phenomenon. For real application, these weaknesses of undoped-BMO-based RRAM devices must be well controlled.

2 Improving resistive switching performance with doping technology

Before discussing the doping effect, we first address the conceivable resistive switching mechanism in BMO-based RRAM. Recent studies have shown that the resistive switching behavior in a BMO-based RRAM device is mainly dominated by the formation/rupture of the conductive filaments inside the BMO layer [18]. The conductive filament is formed by the percolation of defects, such as the migration of metal ions or oxygen vacancies [3]. These defects may come from decomposition of the function materials themselves or diffusion from the electrode materials. However, the generation of these defects in pure BMO films requires a higher voltage. The quality of the films degrades easily under high electrical stimulus, resulting in the poor resistive switching characteristics mentioned above. According to the analysis, if reasonable defects can be introduced into the proper positions in BMO films, high voltage may no longer be necessary and the resistive switching performance can be improved.

2.1 Eliminating the electroforming process and reducing operation voltage

The electroforming operation can induce enough defects (i.e., charge traps, movable ions, or vacancies) in BMO films because of the high electrical voltage. The process is similar to soft-breakdown in an oxide [28]. Under high electrical fields, the induced defects form a local conducting filament between the bottom and top electrodes, resulting in a change in the resistive switching from the HRS to the LRS. However, the high voltage not only degrades the materials reliability, but also complicates the RRAM circuit's design. Thus, the excessive voltage required is undesirable.

By doping proper impurities, the electroforming process can be eliminated and the operation voltage can also be re duced. The *I-V* curve of the Ti doped ZrO_2 device is shown in Figure 2, where the required voltage of the first Set operation is equal to that of the following Set process. Furthermore, the maximum operation voltage of the Cu/ZrO_2/Pt is reduced from 10 to 3 V by doping Ti impurities. It is worth to note that the Cu/ZrO_2:Cu/Pt and Cu/ZrO_2:Cu NC/Pt devices exhibit a similar phenomenon [17,23]. The doping induced forming-free phenomenon has also been observed in other BMO-based RRAMs by other researchers. For example, Gao et al. [28] reported that the average forming voltage of the TiN/HfO_2/Pt device decreased from 7.82 to 2.71 V by doping Al in the HfO_2 films.

Figure 3(a) and (b) shows the typical *I-V* characteristics of the Cu/ZrO_2:Cu/Pt and Cu/ZrO_2:Cu NC/Pt devices, respectively. Both devices exhibit unique nonpolar resistive switching behavior (the Set and Reset operation can be achieved under negative and positive voltages). Different from the Cu/ZrO_2:Cu/Pt device, the Cu/ZrO_2:Cu NC/Pt device exhibits a lower positive Set voltage (the V_{Set} decreased from ~3 to ~1 V). The difference between the two devices can be attributed to the different doping processes. The Cu NC doping process not only supplies more metal ions, but also enhances the electrical field around the Cu NC located within the ZrO_2 matrix. The strengthening electrical field can accelerate the migration velocity of Cu ions and reduce the required voltage to form the conductive filaments [25].

2.2 Improving electrical uniformity

In general, large variations in switching voltages and resistance states are shown in undoped-BMO-based RRAM devices, as can be seen in Figure 1. The poor uniformity not only reduces the stability of the device, but also enhances the complexity of the peripheral circuit for read/write operations. In general, the nonuniformity of the switching parameters is related to the random nature of the nucleation/growth of the conductive filament (CF) [3]. This makes it difficult to form the CF along the same path in repetitive switching cycles.

Compared to the Cu/ZrO_2/Pt device, the Ti doped device shows a more stable Set process, as shown in Figure 2. Further evidence verifying this conclusion is given by the statistical data. As shown in Figure 4, the average values of V_{Set} and V_{Reset} for the Cu/ZrO_2:Ti/Pt device are 1.43 and −0.66 V, respectively, which are lower than the values for the Cu/ZrO_2/Pt device (5.31 and −0.94 V, respectively). Furthermore, the standard deviation of V_{Set} is reduced from 3.45 to 0.78 V after doping Ti ions. This indicates that the dispersion of V_{Set} for the Cu/ZrO_2:Ti/Pt device is obviously reduced when compared with the Cu/ZrO_2/Pt device. The resistance states in 50 cycles of the Cu/ZrO_2/Pt and Cu/ZrO_2:Ti/Pt devices are shown in Figure 5. After doping Ti ions, the fluctuation in R_{HRS} is reduced from 10^4 to 10 times. This proves that the R_{HRS} of the Cu/ZrO_2:Ti/Pt device is more stable than that of the Cu/ZrO_2/Pt device. In addition, the Cu/ZrO_2:Cu/Pt and Cu/ZrO_2:Cu NC/Pt devices also show tight distribution of the resistive switching parameters [17,23].

Previously, improvement in the electrical uniformity of

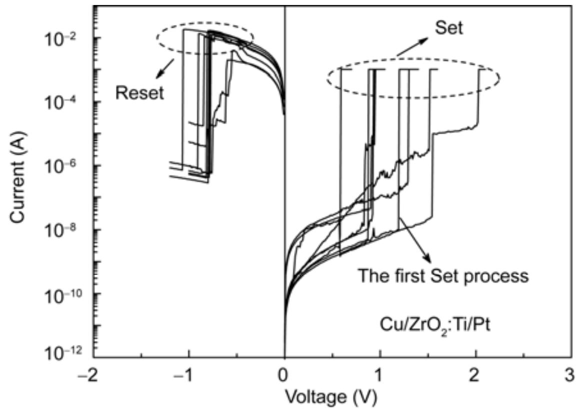

Figure 2 Reproducibility of the resistive switching (10 cycles) of the Cu/ZrO_2:Ti/Pt device under DC voltage sweep. The cell size is 100 μm × 100 μm and the ZrO_2-thinkness is 70 nm.

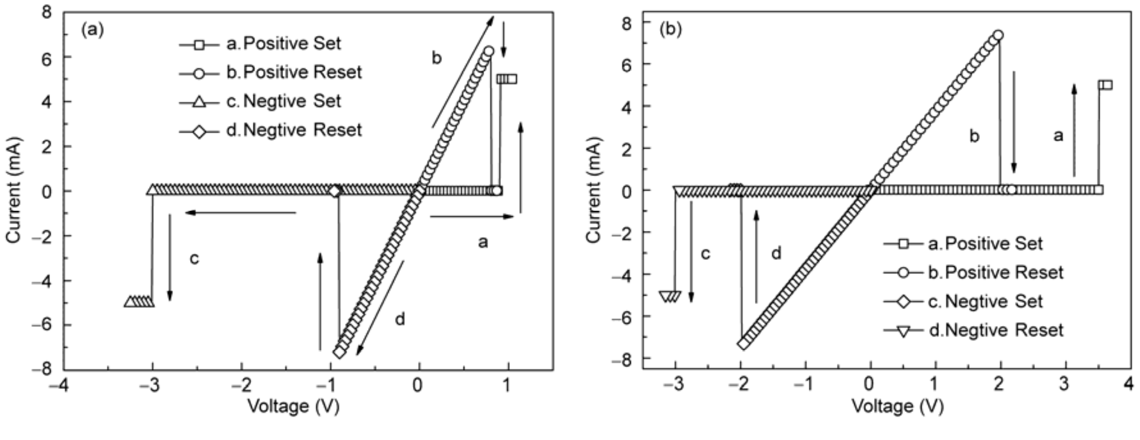

Figure 3 (a) Typical asymmetric nonpolar *I-V* switching behavior of the Cu/ZrO_2:Cu NC/Pt device, and (b) typical symmetric nonpolar *I-V* switching behavior of the Cu/ZrO_2:Cu /Pt device. The cell size of both devices is 3 μm × 3 μm and the thickness of ZrO_2 is 40 nm.

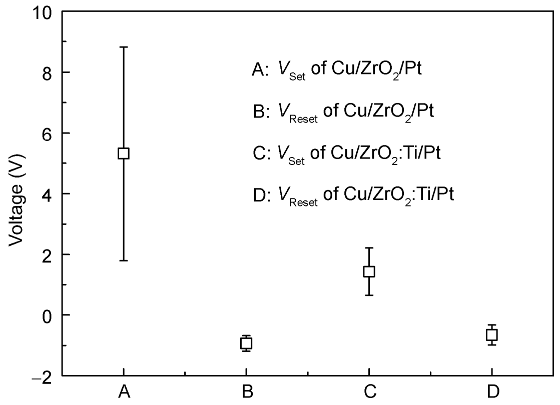

Figure 4 Variations in operating voltage in Cu/ZrO$_2$/Pt and Cu/ZrO$_2$:Ti/Pt devices.

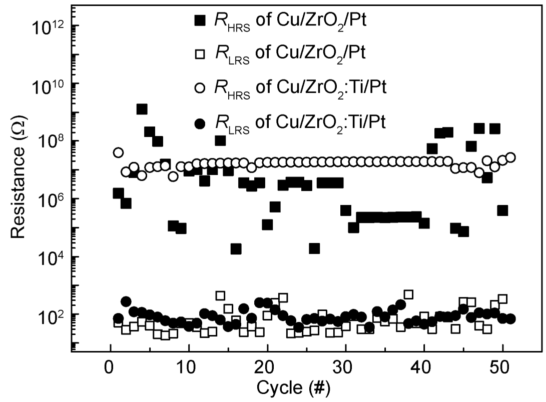

Figure 5 Distribution of R_{HRS} and R_{LRS} in the Cu/ZrO$_2$/Pt and Cu/ZrO$_2$:Ti/Pt devices.

impurities doping in RRAM device has been demonstrated by a variety of studies [17–30]. However, why doping impurities improve the electrical uniformity of the RRAM device is still unclear. A general hypothesis is stated as follows: the conductive filaments are easily formed/ruptured near the impurities doped location. This reduces the randomness of the CF formation/rupture process and improves the uniformity of the resistive switching properties. In our recent work [18], we obtained high resolution transmission electron microscopy images of conductive filaments in the Ag/ZrO$_2$/Cu NC/Pt device. These images show that the growth location and orientation of CFs can be well controlled by the Cu NC dopant. According to the electrical field simulation, the Cu NC plays a critical role in enhancing the local electrical field. During the Set process, more metal ions converge around the Cu NC location under a higher local voltage. So the CF grows easily at the location of the NC. Thus, CFs are easily formed, ruptured, and reformed along the same paths in repetitive switching cycles, resulting in a substantial improvement in the electrical uniformity. For other types of doping impurities, further research is needed to investigate the underlying physical mechanism.

2.3 Increasing device yield

For actual application, device yield (percentage of working cells) is a critical parameter in the memory array. Unfortunately, low device yields are frequently shown in undoped-BMO-based RRAM devices [16,24]. There are two possible reasons for this. One is the electroforming operation, which is needed to activate the resistive switching behavior in undoped devices. During the forming process, the local region of the BMO film may be broken down under high voltage. Another is the randomness of the intrinsic defects in the undoped BMO film. A large variation in the intrinsic defects leads to unstable resistive switching behavior. By using homogeneous and uniform doping, the defects in the BMO film can be well controlled and the device yield is also improved. As can be seen from Figure 6, the device yield of the Cu/ZrO$_2$/Pt device is greatly improved by doping Ti, Cu, and Cu NC. After using doping technology, the device yield of RRAM devices increases to almost 100%. Similar results were also reported by Lee et al. [29] in the Al doped ZnO, Cu doped MoO$_x$ and Cu doped Al$_2$O$_3$ devices.

2.4 Improving other memory performance

Other important memory characteristics of undoped RRAM devices may also be modulated by doping impurities. Recently, Jung et al. demonstrated that Li-doping NiO could improve the thermal stability of the HRS. The Li doped device showed a much better retention property and stable Set/Reset operation [31]. Recently, Wang et al. reported that the retention characteristics of both resistive states in the CuO$_x$-based RRAM can be significantly improved by doping Si impurities. Based on a first principles calculation, they suggested that the activation energy of Cu vacancy migration in Cu$_x$Si$_y$O increased more than that in Cu$_x$O, resulting in the good retention characteristics [32]. In our previous work, we demonstrated that the storage window (defined as the ratio of R_{HRS}/R_{LRS}) of the ZrO$_2$ film can

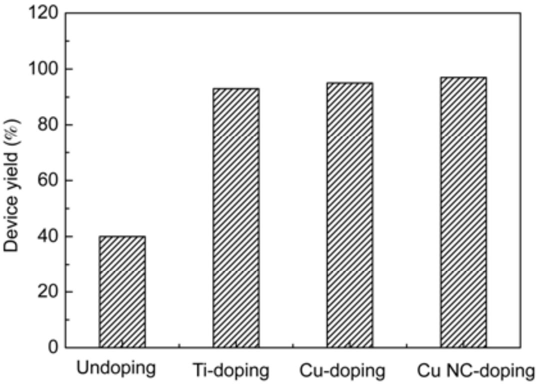

Figure 6 Device yield of the Cu/ZrO$_2$/Pt, Cu/ZrO$_2$:Ti/Pt, Cu/ZrO$_2$:Cu/Pt, and Cu/ZrO$_2$:Cu NC/Pt devices.

Table 1 Resistive switching characteristics of the undoped and doped devices

Device structure	Yield (%)	Forming process	V_{Set} (V)	V_{Reset} (V)	$R_{\mathrm{HRS}}/R_{\mathrm{LRS}}$ ratio	Retention (s)	Switching polarity
Cu/ZrO$_2$/Pt	<40	Yes	0.5–10	–0.5– –1.5	>10^4	–	Bipolar
Cu/ZrO$_2$:Cu/Pt [9]	~100	No	2.1–3.6	0.8–1.5	~10^6	>10^4	Nonpolar
Cu/ZrO$_2$:Au/Pt [33]	~100	No	2–5	0.5–1.2	>10^4	>10^6	Nonpolar
Cu/ZrO$_2$:Ti/Pt [24]	~100	No	1–4	–0.5– –1.5	>10^4	>10^7	Bipolar
Au/ZrO$_2$:Au/Pt [16]	~5	–	–	–	–	–	Bipolar
Au/ZrO$_2$:Au NC /Pt	~75	–	–	–	51	1000	Bipolar
TiN/ZrO$_2$/Pt [28] a)	–	Yes	–	–	100	–	Bipolar
TiN/ZrO$_2$:Al/Pt [28] a)	–	No	0.5–1.5	–0.6– –0.8	100	–	Bipolar
TiN/HfO$_2$/Pt [25] a)	–	–	0.7–2.7	–0.9– –1.5	~3	–	Bipolar
TiN/HfO$_2$:Gd/Pt [25]	–	–	0.8–1.0	–0.6– –0.9	~30	10^4	Bipolar
Pt/TiO$_2$/ Pt [33] a)	–	–	0.25–1.75	–0.25– –0.5	5	1000	Bipolar
Pt/TiO$_2$:Pt NC/Pt a)	–	–	0.5–1.0	–0.5– –0.75	2	10^4	Bipolar
Cu/NiO$_x$/Pt [34] a)	–	Yes	–2.6– –8.6	–1– –1.8	1000	–	Unipolar
Cu/Cu:NiO$_x$ /Pt a)	–	No	–2.1– –3	–0.6– –1	>10	–	Unipolar
W/ZrO$_2$/Pt [35] a)	25	–	–	–	–	–	Unipolar
W/ZrO$_2$:Ag/Pt a)	85	Yes	–	–	10	–	Unipolar

a) Some data are taken from figures in references.

be greatly enhanced by implanting Zr ions [20].

3 Conclusion

The resistive switching characteristics of various devices using doping technology are summarized and shown in Table 1. Compared to an undoped device, the change induced by doping can be observed clearly. In summary, doping technology is an effective method for modulating and improving RRAM's performance. Generally, the doped BMO films exhibit many more preferred memory properties, including a free-electroforming process, low operation voltage, good electrical uniformity, and high device yield. To effectively improve the performance of the RRAM device by doping, more work needs to be done in understanding the physical mechanism and the inherent laws.

This work was supported by the National Basic Research Program of China (2010CB934200, 2008CB925002), the National Natural Science Foundation of China (60825403, 50972160) and the National High-Tech Research & Development Program of China (2008AA031403, 2009AA03Z306).

1 Meijer G I. Who wins the nonvolatile memory race? Science, 2008, 319: 1625–1626

2 Baek I G, Lee M S, Seo S, et al. Highly scalable nonvolatile resistive memory using simple binary oxide driven by asymmetric unipolar voltage pulses. IEDM Tech Dig, 2004: 587–590

3 Waser R, Aono M. Nanoionics-based resistive switching memories. Nat Mater, 2007, 6: 833–840

4 Wang Y, Liu Q, Long S, et al. Investigation of resistive switching in Cu-doped HfO$_2$ thin film for multilevel non-volatile memory applications. Nanotechnology, 2010, 21: 045202

5 Yang Y C, Pan F, Liu Q, et al. Fully room-temperature-fabricated nonvolatile resistive memory for ultrafast and high-density memory application. Nano Lett, 2009, 9: 1636–1643

6 Li Y, Long S, Zhang M, et al. Resistive switching properties of Au/ZrO$_2$/Pt structure for low-voltage nonvolatile memory applications. IEEE Electron Device Lett, 2010, 31: 117–119

7 Xu N, Liu L, Sun X, et al. Characteristics and mechanism of conduction/set process in TiN/ZnO/Pt resistance switching random access memories. Appl Phys Lett, 2008, 92: 232112

8 Lee H Y, Chen P S, Wu T Y, et al. Low power and high speed bipolar switching with a thin reactive Ti buffer layer in robust HfO$_2$ based RRAM. IEDM Tech Dig, 2008: 279–281

9 Guan W, Liu M, Long S, et al. On the resistive switching mechanisms of Cu/ZrO$_2$:Cu/Pt. Appl Phys Lett, 2008, 93: 223506

10 Wu L, Song Z, Liu B, et al. Remarkable resistance change in plasma oxidized TiO$_x$/TiN$_x$ film for memory application. Chin Phys Lett, 2007, 24: 1103–1105

11 Seo S, Lee M J, Seo D H, et al. Reproducible resistance switching in polycrystalline NiO films. Appl Phys Lett, 2004, 85: 5655

12 Sun X, Sun B, Liu L, et al. Resistive switching in CeO$_2$ films for nonvolatile memory application. IEEE Electron Device Lett, 2009, 30: 334–336

13 Banno N, Sakamoto I, Sunamura H, et al. Diffusivity of Cu ions in solid electrolyte and its effect on the performance of nanometer-scale switch. IEEE Trans Electron Device, 2008, 55: 3283–3287

14 Lv H, Wang M, Wan H, et al. Endurance enhancement of Cu-oxide based resistive switching memory with Al top electrode. Appl Phys Lett, 2009, 94: 213502

15 Li Y, Long S, Liu Q, et al. Nonvolatile multilevel memory effect in Cu/WO$_3$/Pt device structures. Phys Status Solidi RRL, 2010, 4: 124–126

16 Guan W, Long S, Jia R, et al. Nonvolatile resistive switching memory utilizing gold nanocrystals embedded in zirconium oxide. Appl Phys Lett, 2007, 91: 062111

17 Liu Q, Long S B, Wang W, et al. Low-power and highly uniform switching in ZrO$_2$-based ReRAM with a Cu nanocrystal insertion layer. IEEE Electron Device Lett, 2010, 31: 1299–1301

18 Liu Q, Long S, Lv H, et al. Controllable growth of nanoscale conductive filaments in solid-electrolyte-based ReRAM by using a metal nanocrystal covered bottom electrode. ACS Nano, 2010, 4: 6162–6168

19 Yoon J H, Kim K M, Lee M H, et al. Role of Ru nano-dots embedded

in TiO_2 thin films for improving the resistive switching behavior. Appl Phys Lett, 2010, 97: 232904

20 Liu Q, Guan W H, Long S B, et al. Resistive switching memory effect of ZrO_2 films with Zr^+ implanted. Appl Phys Lett, 2008, 92: 012117

21 Wong M F, Herng T S, Zhang Z, et al. Stable bipolar surface potential behavior of copper-doped zinc oxide films studied by Kelvin probe force microscopy. Appl Phys Lett, 2010, 97: 232103

22 Liu Q, Guan W H, Long S B, et al. Resistive switching of Au-implanted-ZrO_2 film for nonvolatile memory application. J Appl Phys, 2008, 104: 114514

23 Guan W, Long S, Liu Q, et al. Nonpolar nonvolatile resistive switching in Cu doped ZrO_2. IEEE Electron Device Lett, 2008, 29: 434–437

24 Liu Q, Long S B, Wang W, et al. Improvement of resistive switching properties in ZrO_2-based ReRAM with implanted Ti ions. IEEE Electron Device Lett, 2009, 30: 1335–1337

25 Zhang H, Liu L, Gao B, et al. Gd-doping effect on performance of HfO_2 based resistive switching memory devices using implantation approach. Appl Phys Lett, 2011, 98: 042105

26 Zhang H, Gao B, Sun B, et al. Ionic doping effect in ZrO_2 resistive switching memory. Appl Phys Lett, 2011, 96: 123502

27 Dearnaley G, Stoneham A M, Morgan D V. Electrical phenomena in amorphous oxide films. Rep Prog Phys, 1970, 33:1129

28 Gao B, Zhang H, Yu S, et al. Oxide-based RRAM: Uniformity improvement using a new material-oriented methodology. VLSI Tech Dig, 2009: 30–31

29 Lee D, Seong D, Choi H, et al. Excellent uniformity and reproducible resistance switching characteristics of doped binary metal oxides for non-volatile resistance memory applications. IEDM Tech Dig, 2006: 797

30 Jung K, Choi J, Kim Y, et al. Resistance switching characteristics in Li-doped NiO. J Appl Phys, 2008, 103: 034504

31 Wang M, Luo W J, Wang Y, et al. A novel Cu_xSi_yO resistive memory in logic technology with excellent data retention and resistance distribution for embedded applications. VLSI Tech Dig, 2010: 89–90

32 Liu Q, Liu M, Long S B, et al. Improvement of resistive switching properties in ZrO_2-based ReRAM with implanted metal ions. In: Proceeding of the European Solid-State Device Research Conference, 2009 Sep 14–18, Athens. 221–224

33 Chang W, Cheng K, Tsai J, et al. Improvement of resistive switching characteristics in TiO_2 thin films with embedded Pt nanocrystals. Appl Phys Lett, 2009, 95: 042104

34 Liu C, Lin X, Wang H, et al. Improved resistive switching dispersion of NiO_x thin film by Cu-doping method. Jpn Appl Phys Lett, 2010, 49: 056507

35 Sun B, Liu L, Han D, et al. Improved resistive switching characteristics of Ag-doped ZrO_2 films fabricated by sol-gel process. Chin Phys Lett, 2008, 25: 2