Research Article

Bipolar Switching Characteristics of RRAM Cells with $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ Film

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The electrical conduction and bipolar switching properties of resistive random access memory (RRAM) cells with transparent calcium bismuth titanate ($\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ —CBTi44) thin films were investigated. Experimentally, the (119)-oriented CBTi44 thin films were deposited onto the ITO/glass substrates by RF magnetron sputtering followed by rapid thermal annealing (RTA) at a temperature range of 450–550°C. The surface morphologies and crystal structures of the CBTi44 thin films were examined by using field-emission scanning electron microscopy and X-ray diffraction measurements. The on/off ratio and switching behaviors of the transparent Al/CBTi44/ITO/glass RRAM devices were further discussed in this work.

1. Introduction

Recently, various new nonvolatile memory devices were investigated, such as ferroelectric random access memory (FeRAM), resistive random access memory (RRAM), and phase change memory (PCM). Especially, the RRAM that composed of a simple metal-insulator-metal (MIM) structure has the advantages of low power consumption, high speed operation, good retention, and high-density integration capability [1–3]. Recent RRAM research includes perovskite oxides and metal oxides with different electrodes such as VO [4], $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ [5], NiO [6], La_2O_3 [7], Dy_2O_3 [8], and ZnO [9].

Several perovskite materials, such as $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ (SBT) [10], $(\text{Ba}_{0.7}\text{Sr}_{0.3})(\text{Ti}_{0.9}\text{Zr}_{0.1})\text{O}_3$ [11], $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ (CBT) [12, 13], $\text{CaBi}_{4-x}\text{Nd}_x\text{Ti}_4\text{O}_{15}$ (CBNT) [14], and $\text{Ca}_{1-x}\text{La}_x\text{Bi}_4(\text{Ti}_{0.9}\text{W}_{0.1})_4\text{O}_{15}$ (CLBTW) [15], have been developed and investigated recently. Especially, the CBT film has high Curie temperature and low current density [16, 17]. In this study, we have investigated the bipolar resistive switching properties of the CBTi44 thin films in the metal-insulator-metal (MIM) structure for memory application.

2. Experiment

In this study, the CBTi44 thin films were deposited onto the ITO/glass substrates by RF magnetron sputtering with a ceramic CBTi44 target. Ceramic target of CBTi44 was prepared by conventional solid-state reaction technique. First, raw materials of Bi_2O_3 , CaO, and TiO_2 were weighted first according to the stoichiometric ratio of $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$. After mixing of the raw materials, the mixed material was ball-milled for 5 h. The mixture was then dried and calcined at 1100°C for 4 h. Finally, the CBTi44 target was formed with a diameter of 2 inches. The CBTi44 films of 300 nm thickness were then deposited onto the ITO/glass substrates by RF magnetron sputtering with the CBTi44 target. The preparation conditions of the CBTi44 thin films are summarized in Table 1. To form the transparent MIM Al/CBTi44/ITO/glass RRAM device structure as shown in Figure 1, the top Al electrodes were patterned using a metal mask and deposited on top of the CBTi44 film by thermal evaporation. The phase and the surface morphology of the deposited CBTi44 films were characterized by X-ray diffraction (XRD) and field-emission scanning electron microscopy (FE-SEM). The

FIGURE 1: Metal-insulator-metal (MIM) capacitor structure of the CBTi144 RRAM device.

FIGURE 2: Surface morphologies of the CBTi144 films with (a) no annealing, (b) 450°C RTA, (c) 500°C RTA, and (d) 550°C RTA.

leakage current characteristics of the CBTi144 thin films were measured by a gain phase analyzer (HP4156C).

3. Results and Discussion

Figure 2 shows the FE-SEM micrographs of the CBTi144 thin films without annealing and with rapid thermal annealing (RTA) at 450, 500, and 550°C. As the annealing temperature is

increased, the grain size of the CBTi144 film slightly increases and the porosity of the CBTi144 film decreases because the oxygen vacancy concentration in the CBTi144 film decreases [18].

Figure 3 shows the XRD patterns of the CBTi144 thin films without and with 450–550°C RTA. The XRD patterns were used to identify the changes on crystalline structures of annealed CBT thin films. The results of the XRD analysis

FIGURE 3: XRD patterns of the CBTi44 thin films with different annealing temperatures.

FIGURE 4: XPS of the CBTi44 thin films with different annealing temperatures: (a) Ca 2p3/2, (b) Bi 4f7/2, (c) Ti 2p3/2, and (d) O 1s.

FIGURE 5: I - V characteristics of the CBTi144 RRAM cell without and with 450–550°C RTA.

(a)

(b)

(c)

FIGURE 6: Current conduction mechanisms of the Al/CBTi144/ITO/glass RRAM cell annealed at 450°C: (a) in the entire switching operation, (b) during the Set process, and (c) during the Reset process.

FIGURE 7: Endurance test of the Al/CBT/ITO/glass cell with different CBT annealing conditions: (a) as-deposited, (b) 450°C annealed, (c) 500°C annealed, and (d) 550°C annealed.

show that the CBT films are of polycrystalline and the peaks of the XRD patterns correspond to the (006), (008), (119), (2010), and (220) orientations of the perovskite crystal [19]. As the annealing is increased, most of the intensities of the XRD peaks increase. This indicates that the grain sizes of the CBT films increase with the RTA temperature.

Figure 4 shows the XPS analysis of the CBTi144 thin films with different annealing conditions. It is noted that the amounts of all the compositional elements in the CBT films decrease as the annealing temperature increases. The oxygen content decreases slightly for the cases of 450°C and 500°C annealing that the oxygen vacancies may increase accordingly. However, as the annealing temperature increased to 550°C which is close to the melting point of the glass substrate, the oxygen content decreases drastically presumably due to the increased stress between the CBT film and the ITO/glass substrate.

Figure 5 shows the current-voltage (*I-V*) characteristics of the CBTi144 thin films without and with 450–550°C RTA. From the *I-V* measurement, the CBTi144 thin films show good nonvolatile resistive switching properties. The transport current of the CBTi144 thin film increases as the RTA temperature increases up to 450°C. However, the transport current of the CBTi144 films will decrease if the RTA temperature is increased to 500°C and 550°C. When the annealing temperature increases, the concentration of the oxygen vacancies in the CBTi144 thin film reduces that the bipolar resistive switching characteristics of the CBTi144 RRAM structure will deteriorate.

Figure 6(a) shows the *I-V* characteristics of the transparent Al/CBTi144/ITO/glass RRAM cell exhibiting bipolar resistive switching behavior with different conduction mechanisms during the switching operation. With RTA temperature of 450°C, the *I-V* characteristics of the CBTi144 RRAM

TABLE 1

Target diameter (inch)	2
Substrate temperature (°C)	30
RF power (W)	100
Chamber pressure (mTorr)	20
Oxygen concentration (%)	0
Deposition time (h)	2
Annealing temperature (°C)	450–550

cell exhibit large on/off ratio over 100 at a bias voltage of 0.1 V. There are two conduction mechanisms, the Ohm's law (I/V) and the trap-filled limit (I/V_n), dominant during the Set process of the RRAM cell, as shown in Figure 6(b). The thermally generated carrier density is higher than the injected carrier density in the low bias regime [7, 8]. Therefore, the Ohm's law mechanism dominates the conduction behavior in the low bias regime. The SCLC characteristics include the Ohm's law ($I \propto V$), the trap-filled limit behavior, and the Child's law ($I \propto V^2$) [7, 8]. However, the HRS has two kinds of conduction mechanisms in the high bias regime where the trap model with space-charge-limited conduction (SCLC) is dominant [20]. Figure 6(c) shows the current conduction mechanisms during the Reset process of the RRAM cell. In the LRS and HRS, the Reset process has similar conduction mechanisms to the Set process.

Figure 7 shows the endurance characteristics of the Al/CBT/ITO/glass cells with different annealing conditions. For the case of 450°C annealing as shown in Figure 7(b), the endurance characteristics of the cell in the first 10 continuous switching cycles still show an HRS/LRS ratio of 100. But after 10 continuous switching cycles, the cell shows an unstable HRS/LRS ratio. For the case of 500°C and 550°C annealing as shown in Figures 7(c) and 7(d), the HRS/LRS ratio is even degraded. It is mainly because of the large reduction in oxygen content at higher annealing temperatures that the cell cannot switch properly in the HRS and LRS.

4. Conclusions

In this work, the resistive switching behavior of the transparent Al/CBTi144/ITO/glass RRAM cells has been investigated. Our results show that the conduction switching behavior of the CBTi144 RRAM cells is of bipolar switching. The current conduction mechanisms of the CBTi144 RRAM cells have also been discussed in this work.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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