ORIGINAL PAPER

Forming-Free Unipolar Resistive Switching in $BiFe_{0.95}Co_{0.05}O_3$ Films

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Abstract We report the forming-free unipolar resistive switching effects in polycrystalline $BiFe_{0.95}Co_{0.05}O_3$ films which were spin-coated on ITO/glass substrates by a chemical solution deposition method. The resistive ratio of the high resistive state (HRS) to the low resistive state (LRS) is more than 2 orders of magnitude. The conduction of the HRS is dominated by the space-charge-limited conduction mechanism, while Ohmic behavior dominates the LRS, which suggests a filamentary conduction mechanism. The oxygen vacancies are considered to play an important role in forming the conducting filaments.

1 Introduction

The resistive random access memory (RRAM) is based on the electrical field induced reproducible resistance change between the high resistive state (HRS) and low resistive state (LRS). RRAM has been demonstrated to possess advantages such as low-power consumption, high-speed operation, and high-density integration, which has been considered to be one of the key technological steps to extend the functional equivalence of Moore's law [1, 2]. Unipolar and bipolar resistive switching processes have been commonly observed in binary and perovskite oxide materials, e.g. ZnO [3], SiO_2 [4], $SrTiO_3$ [5], etc.

$BiFeO_3$ is a widely studied multiferroic material for its above room temperature ferroelectric Curie temperature ($T_C \sim 1103$ K) and antiferromagnetic Néel temperature ($T_N \sim 643$ K) [6]. Recently, bipolar resistive switching behavior has been observed in $BiFeO_3$ and its derivatives [7–11]. However, the mechanism is still under debate. Various mechanisms have been suggested, including the ionic and electric conduction by the redistribution of oxygen vacancies [7, 8], the diffusion of metal electrodes [9], and the control of the extension of the depleted space charge region of Schottky contacts [10, 11]. Furthermore, unipolar resistive switching is generally observed in oxides, however, rarely in $BiFeO_3$ and generally a forming process is needed [2]. In this paper, we report the forming-free unipolar resistive switching in $BiFe_{0.95}Co_{0.05}O_3$ films and confirm that oxygen vacancies play an important role in forming the conducting filaments. The formation and rupture of the conducting filaments are responsible for the unipolar resistive switching in $BiFe_{0.95}Co_{0.05}O_3$ films.

2 Experimental Details

$Bi(Fe_{0.95}Co_{0.05})O_3$ films were deposited onto conductive indium tin oxide (ITO)/glass substrates by a chemical solution deposition method. The precursors were prepared by dissolving $Bi(NO_3)_3 \cdot 5H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ in acetic acid and methanol. Ethylene glycol was added to adjust the viscosity. Citrate acid was added as

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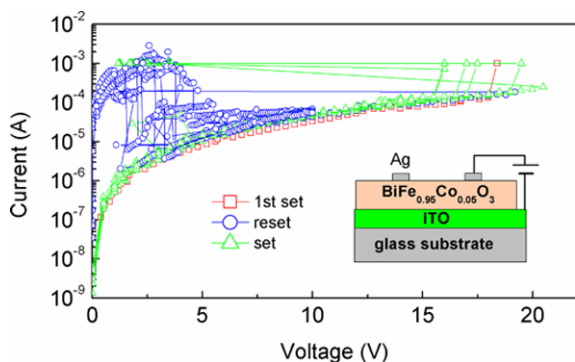
Fig. 1 Typical resistive switching characteristics of a Ag/BiFe$_{0.95}$Co$_{0.05}$O$_3$/ITO device with positive bias applied on the top electrode

Fig. 2 Retention of HRS and LRS for a Ag/BiFe$_{0.95}$Co$_{0.05}$O$_3$/ITO device at room temperature with bias voltage of 0.5 V

the chelating agent. The Bi(Fe$_{0.95}$Co$_{0.05}$)O$_3$ films were deposited onto the substrates by spin coating at 4000 rpm for 30 s. The wet films were pyrolyzed at 400 °C for 10 min in O$_2$ and annealed at 525 °C for 5 min in N$_2$. These steps were repeated several times to increase the thickness of the films. The films have been finally annealed at 525 °C for 30 min in N$_2$ for achieving the better crystallinity. The X-ray diffraction (XRD) with Cu Kα radiation was used for the phase analysis, and the films exhibit R3c structure without any impurity phase [12]. The thickness of the films was determined to be about 240 nm from the cross-sectional scanning electron microscopy (SEM) image. Clear ferroelectricity with a remnant polarization value of about 22 μC/cm^2 at room temperature has been observed [12]. The current–voltage (I–V) measurements were carried out using a Keithley 2400 SourceMeter and 2182A Nanovoltmeter. Silver glue dots with a diameter of ca. 1 mm were used as top electrodes. The schematic Ag/BiFe$_{0.95}$Co$_{0.05}$O$_3$/ITO device structure is illustrated in the inset of Fig. 1. During the voltage sweep mode, the bias was defined as positive when the current flowed from the top electrode through the film to the bottom ITO electrode.

3 Results and Discussions

The I–V cycles of a Ag/BiFe$_{0.95}$Co$_{0.05}$O$_3$/ITO device are plotted in Fig. 1. The device is initially in the HRS. By sweeping the bias voltage to a certain value, the device in the HRS will switch to the LRS via the set process. As the device turns to the LRS, the current suddenly increases, and the voltage across the device reduces due to a larger voltage drop across the series resistor. To protect the devices, a compliance current of 1 mA was selected for the set processes. A subsequent sweep without compliance current will switch the device back to the HRS, which is called the reset process. All the sweeping sequences from 0 V to the maximum voltage were finished within 10 s. As can be seen, the
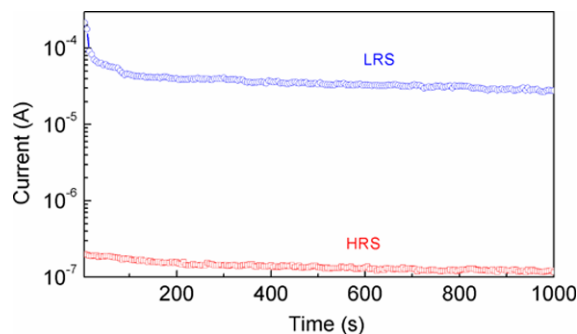
device exhibits the typical characteristics of unipolar resistive switching. The device switched to the LRS at voltage V_{set} in the range from 15 V to 21 V, while in the subsequent reset processes, the device switched to the HRS at voltage V_{reset} in the range from 1 V to 8 V. Generally, the 1st set process is called forming process, which needs higher voltage to switch the devices from HRS to LRS than that in the subsequent set processes [13, 14]. Furthermore, the initial resistance in forming process is much higher than the resistance in the following set processes [14–16]. As can be seen in Fig. 1, the 1st V_{set} is about 18 V, which is in the range of subsequent V_{set}. And the resistance in the 1st set process is almost the same as that in the following set processes. Thus no significant difference between the 1st set process and the subsequent set processes can be observed, and we can call this the forming-free unipolar resistive switching [16]. This is in contrast to the previous reported unipolar resistive switching with a forming process in BiFeO$_3$ films [2].

The data retention characteristics of Ag/BiFe$_{0.95}$Co$_{0.05}$O$_3$/ITO devices in HRS and LRS were measured by the current under applied bias voltage of 0.5 V, as shown in Fig. 2. The resistance ratio of the HRS to the LRS is more than 2 orders. Though a gradual decrease of the current can be observed indicating the gradual increase of the resistance in the beginning of the measurement in the LRS, no significant change of resistance ratio in the HRS and the LRS was observed after 1000 s, indicating the good data retention characteristics.

To gain more insight into the unipolar resistive switching, the conduction mechanisms for the HRS and the LRS are analyzed, and the typical I–V curves of the set and reset processes are plotted in the log-log scale, as shown in Fig. 3. The I–V curves exhibit a linear Ohmic behavior with a slope of 1.07. This is consistent with the conducting filament model [17, 18]. However, the conduction mechanisms of the devices in the HRS are more complicated. Fitting results of the HRS suggest that the leakage current in the low-voltage range shows a linear dependence on voltage with a slope of 1.08, corresponding to the Ohmic conduction. While in
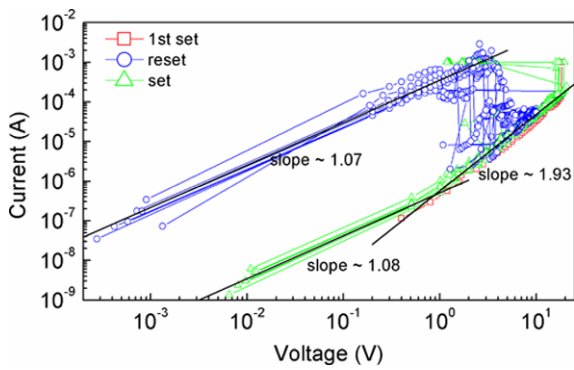
Fig. 3 The log–log plot of $I-V$ curves of a $Ag/BiFe_{0.95}Co_{0.05}O_3/ITO$ device with positive bias applied on the top electrode
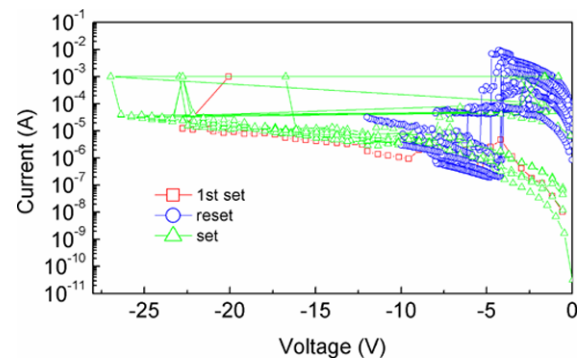

Fig. 4 Typical resistive switching characteristics of a $Ag/BiFe_{0.95}Co_{0.05}O_3/ITO$ device with negative bias applied on the top electrode

the high-voltage range, a current square-dependence on voltage with a slope of 1.93 can be observed, corresponding to the typical trap-controlled space charge limited conduction (SCLC) [17–20]. This further suggests that the high conductivity in the LRS should be a confined, filamentary effect [18].

The filamentary model can be used to explain the resistive switching phenomenon in the devices. However, the formation of the filaments should be clarified. Li attributed the formation of the conducting filaments to the metal ions diffusing from the metallic electrodes [9]. Due to the Ag top electrode used in the measurements, Ag ions might first be oxidized to Ag^+, and migrate toward the bottom electrode and reduce there by electrons flowing from the cathode. The successive precipitations of Ag metal atoms finally form the conducting filaments [9, 18]. To check the possibility of the metal filaments, we selected another pristine device, and applied the negative voltage on the top electrode. Due to the asymmetric structure of the device, Ag^+ from the top electrode will not migrate to the bottom electrode with negative voltage applied on the top electrode to form the conducting filaments, thus the resistive switching process should be different from that with the positive voltage applied on the top electrode. The $I-V$ curves with negative bias on the top electrode are shown in Fig. 4. As can be seen, similar phenomenon as that with positive bias applied on the top electrode has been observed. The 1st V_{set} is in the range of subsequent V_{set}, and the resistance in the 1st set process is almost the same as that in the following set processes. Also the V_{set} and V_{reset} are almost the same as those with positive bias. Thus the metallic filaments due to the diffusion of the metal ions from the top electrode can be excluded.

Here, we attribute the formation of the conducting filaments to the diffusion of oxygen vacancies under the electric field. In $BiFeO_3$, oxygen vacancies are always observed, since the Fe^{2+} can be clearly resolved even in the powders sintered in air [21]. The mixed valence state of Fe^{3+} and Fe^{2+} and the possible hopping of electrons from site to

site are generally considered as the leakage current mechanism [22]. The electrons originated from deep-level traps in the band gap which can be induced by oxygen vacancies [23]. The pristine $BiFe_{0.95}Co_{0.05}O_3$ film is most likely to be in the HRS due to the large grain boundary resistance [8]. Under high electric field in the set processes, conduction paths might be formed due to the redistribution of the oxygen vacancies under the high electric field, and the devices switch to the LRS. The reset processes are thermally driven by current-local-heating, as can be seen from the broad distribution in the reset processes [24]. In reset processes, large current is applied through the conducting filaments in the devices, and the Joule heating might lead to the local elemental composition change so that some oxygen vacancies are occupied by oxygen ions, thus the filament is ruptured and the devices switch from the LRS to the HRS [16]. The forming-free resistive switching might be attributed to the pre-existing oxygen vacancies [14, 16]. In our sample, high concentration of oxygen vacancies might be expected due to the annealing in N_2 atmosphere. The redistribution of oxygen vacancies in the grain boundaries to form the conducting filaments in the 1st and subsequent set processes might be almost the same, thus the voltage required in the first HRS to LRS switching could be reduced, leading to the forming-free unipolar resistive switching.

To confirm the role of oxygen vacancies in the resistive switching, we annealed one $BiFe_{0.95}Co_{0.05}O_3$ film in air at 500 °C for 30 min, and then the same device structure with Ag dots as top electrodes were fabricated. The annealing can effectively decrease the concentration of the oxygen vacancies [23], which is confirmed by the much larger resistance in the 1st set process than that in the pristine devices (Fig. 5). The device changes from the HRS to the LRS at around 6 V (a compliance current of 1 mA was set), which is much smaller than the V_{set} (15 V to 21 V) of pristine devices (Fig. 2). However, this is an irreversible process, as no change from the LRS to the HRS can be observed and the current in the LRS continuous to increase with increas-
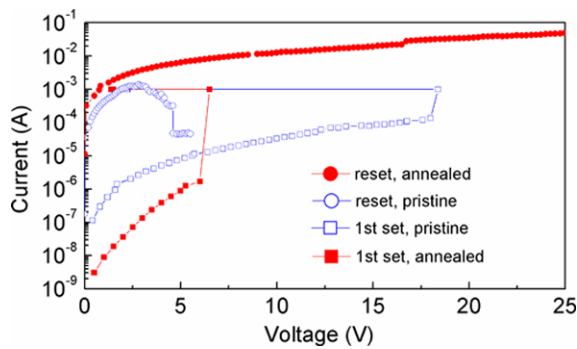
Fig. 5 I–V characteristics of Ag/BiFe$_{0.95}$Co$_{0.05}$O$_3$/ITO devices with the BiFe$_{0.95}$Co$_{0.05}$O$_3$ film annealed in air at 500 °C for 30 min (*filled symbols*) and the pristine BiFe$_{0.95}$Co$_{0.05}$O$_3$ film (*open symbols*, from Fig. 1)

ing voltage up to 25 V. Thus conducting filaments cannot be formed without sufficient high concentration of oxygen vacancies.

4 Conclusions

In summary, polycrystalline BiFe$_{0.95}$Co$_{0.05}$O$_3$ films were spin-coated on ITO/glass substrates by a chemical solution deposition method. The forming-free unipolar resistive switching behavior has been demonstrated. The resistive ratio of the HRS to the LRS is more than 2 orders of magnitude. The dominant conduction mechanism of the LRS and the HRS are Ohmic behavior and trap-controlled SCLC, respectively. The observed resistive switching behavior could be attributed to the filamentary conduction mechanism, and the redistribution of oxygen vacancies in the grain boundaries under an electrical field plays an important role in forming the conducting filaments.

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