The transformation of digital to analog resistance switching behavior in Bi$_2$FeCrO$_6$ thin films

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ABSTRACT

Bi$_2$FeCrO$_6$ (BFCO) thin films were fabricated by sol-gel method. Digital and analog resistive switching behaviors were sequentially observed in Au/BFCO/FTO/Glass structure by applying a continuous cyclic voltage. By analyzing formation mechanism of the two types of the resistive switching behaviors, it is found that the digital resistive behavior conductance mechanism is a bulk-limited conduction, and the analog resistive switching behavior is accompanied with rectification effects and negative differential resistance behaviors, which are considered as interface-limited conductivity behaviors. So the change of digital and analog resistive switching behaviors may be result of the transformation of conductive mechanism. These research results will help us to design and manufacture digital and analog multifunctional resistive switching memory devices.

1. Introduction

Resistive random access memory (RRAM) is a candidate for a new type of nonvolatile memory (NVM) devices owing to its fast running speed, high storage density, low power consumption [1–4]. RRAM is based on the resistive switching (RS) behavior and could implement memory functions by controlling the switching of high resistance state (HRS) and low resistance state (LRS) to represent 0 and 1 in the computer binary [5–7]. The RS behavior can be divided into digital and analog types [8–10]. The resistance of digital RS devices will change abruptly, and the different states generated are mostly used for information storage. Usually, the formation and fracture of metal or oxygen vacancies conductive filaments are used to explain such type resistance behavior. In contrast, it is an analog type of RS behavior in which resistance is gradually transformed. This RS behavior can not only be used for information storage, but also can be used to achieve synaptic functions to achieve functions such as brain-inspired neuromorphic computing. Although various physical models have been established to explain this resistance change behavior, such as the Schottky barrier model for polarization or charge defect regulation, the charge trap charge-discharge model, and the ferroelectric tunnel junction, etc [11–14]. The physical mechanism is still unclear. In general, digital and analog resistance change behaviors only exist in separate devices, but devices that integrate digital and analog functions at the same time will greatly reduce the complexity of the device and enhance the anti-interference ability. There are few reports on the multi-function digital and analog resistance-to-change function of a single memory, and the switching mechanism is not clear, which deserves more research and attention. Bi$_2$FeCrO$_6$ (BFCO), as a double perovskite ferroelectric material, has excellent multiferoic and photoelectric properties, so BFCO has special properties. Resistive behaviors have also been studied as potential applications [15].

In this work, Bi$_2$FeCrO$_6$ thin films were coated on SnO$_2$F (FTO) glass substrates by sol-gel method [16], and digital and analog resistive switching behaviors were sequentially observed in Au/BFCO/FTO/Glass structure. By analyzing the mechanism of the two types of RS behaviors, the influence of oxygen vacancy and interface effect on the two kinds of RS behavior is explained, and the reason of digital to analog RS behavior is analyzed.

2. Materials and methods

Bi$_2$FeCrO$_6$ (BFCO) thin films were prepared by coating on industrially produced FTO glass substrates. The BFCO precursor solutions were prepared from Bi(NO$_3$)$_3$·5H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O and Cr(NO$_3$)$_3$·9H$_2$O. CH$_3$COOH and CH$_3$CH$_2$CH$_2$OH were chosen as solvent, C$_6$H$_5$O$_2$ as stabilizer. And add the appropriate amount of HOCH$_2$CH$_3$NH$_2$ to adjust the pH to 5. Considering the loss of bismuth in the deposition
process, 5% Bi(NO₃)₃ · 5H₂O excess was added in the precursor solutions. Stirred the prepared solution at room temperature for 2 hours to ensure that the raw material is completely dissolved and gelled. Filtered and bottled, the precursor solutions will be placed for a week to ensure formation the BFCO sol-gel. The precursor solutions were uniformly deposited on the FTO conductive glass under the rotation at the speed of 6000 rpm by 16 s and then the wet thin films were placed on a 300°C heating stage for baking for about 10 minutes to promote thermal decomposition and crystal growth. Repeat the above steps until the films of appropriate thickness are obtained. Finally, the films were heat-treated in air atmosphere at 650 °C for 15 min.

Grazing incidence X-ray diffraction (GIXRD, D/MAXUltima IV) was used to analyze the crystal structure of the films. Scanning electron microscope (SEM, Hitachi S3400NII) is used to observe the morphology and structure of film surface and cross section. CurrentVoltage curve (IV curve) were measured by the Keithley 2400 programmable electrometer (Tektronix Company, USA). The ferroelectric properties of thin film were characterized by ferroelectric tester (Precision Premier II, USA).

3. Results and discussion

Figure 1(a) shows the GIXRD pattern of the BFCO thin film growth on FTO/Glass substrate by a sol-gel method. It can be seen that the resulting film is polycrystalline. Most of the peaks can be attributed to the rhombohedral distorted perovskite structure of BFCO, belong to R3c space group. Meanwhile, several peaks of Bi₂O₃ can be observed, marked by green triangle sign in the figure, which can be attributed to the excessive Bi in the process of preparation. It can also be observed from the figure that the obvious space group of (Fe,Co)₃O₄ is Fd3m diffraction peak, which is represented by blue diamond sign in the figure. This is due to the fact that (Fe,Co)₃O₄ is easier to crystallize than BFCO, at lower annealing temperatures. These results show that the films are composed of at least three kinds of crystals. Therefore, the subsequent properties of the film may be the result of the joint action of the three components.

The SEM images of the surface and section morphology of BFCO thin film are shown in Figure 1(b). The thin film is in good crystal condition, and the whole surface is dense and flat. It is worth noting that there are large grains with a diameter of about 200 nm on the surface of the thin film, which may be compose of multiple crystallites. The inset of Figure 1(b) shows the section structure of BFCO thin film coated on FTO glass. The sandwich structure composes of glass, FTO and BFCO thin film is clearly visible. And the thickness of the thin film is about 200 nm. There are also obvious large grain bulges on the cross-section images, which correspond to the large grains in the surface morphology.

To study RS behavior, a scanning voltage of 0→6→0→6→0 V is continuously applied to the device, and the change of I–V curve is shown in Figure 2. The main diagram shows the logarithmic coordinates of the I–V curve, and the right inset shows the corresponding linear coordinates. The left inset shows the measurement schematic diagram of Au/BFCO/FTO structure device with Au as the electrode, and subsequent data are all measured under this structure. As shown in Figure 2(a), the device is initially exhibit the first type of RS behavior (digital) in HRS, with the increasing of negative voltage gradually, the device resistance suddenly set to the LRS. In order to protect the device from permanent breakdown, a 10 mA limiting current is applied at the negative voltage. Then the device can be reset to HRS by applying an enough positive bias. The memory ON/OFF ratio of this type of RS behavior reached 10⁳. After about 70 cycles (See Figure S1 in supplementary material), the digital RS behavior gradually disappeared and the subsequent state shown in Figure 2(b). In this state, 1,2,3 and 4 in the device cycle correspond to LRS, HRS, LRS and HRS, respectively. The former resistance state cannot affect the next resistance state, so the device has memoryless effect. As the increase of the cycle times, the second type of RS behavior (analog) has been exhibited, as
shown in Figure 2(c and d). It should be noted that the HRS of the first type of resistance becomes the LRS of this type of resistance. And the device displays HRS, LRS, LRS and HRS corresponding to 1, 2, 3 and 4 sequence respectively, which is completely opposite to the first type of RS behavior. The resistive change of this RS behavior is not steep and there is no obvious jump process. All of these show that the physical mechanism of RS behavior has changed. The analog RS behavior is more stable (see Figure S2 in supplementary material). And the memory ON/OFF ratio is gradually increased to $10^3$. It should be noted that, with the change of resistance state, the typical diode rectification effect and negative differential resistance (NDR) is accompanied.

In order to clarify the internal factors that lead to the transformation of digital to analog RS behaviors, we have studied the physical mechanisms that produce these two types of resistive change. For the digital RS behavior, the function of Log(V) and Log(I) was used to investigate the conduction mechanism. The $I-V$ curves of the positive and negative bias regions in the logarithmic coordinates are shown in Figure 3(a and b), “K” represents the slope. For the negative bias region in the HRS, the low-pressure region Log(I) has a linear relationship, and the slope is 1.13. This is in line with the Ohmic conduction mechanism ($I \propto V$) [17–19], with the increase of voltage, slope could up to 2.25 and 2.00, it is in accordance with the Child’s law ($I \propto V^2$) [20,21], followed by a large slope of the jump behavior, the sample set to LHS. As the voltage decreases, the Ohmic conduction mechanism is restored. The same transition law is applied to the positive bias region, the Ohmic conduction is performed at low voltage, and the Child’s law is met at high voltage, a jump process with large slope between HRS and LRS, which is consistent with the mechanism of trap-controlled Space-Charge-Limited-Conduction (SCLC) [22,23]. Since Ohmic conductance and SCLC conductance are both bulk-limited conductance mechanisms, it can be judged that the first type RS behavior is caused the generation and fracture of oxygen vacancy conductive filaments (CF) [24–26].

Based on the above analysis, it can be inferred that the cause of the first type RS behavior is the generation and fracture of oxygen vacancy CF. As shown in Figure 3(c), in the initial state, there are enough oxygen...
vacancies are randomly distributed in the BFCO thin films layer. When a negative bias is applied in the Au electrodes, the oxygen vacancies are concentrated toward the Au electrode under the action of the electric field to form a plurality of CF, and finally only one CF is in contact with the FTO, the thin film is set to LRS, this process corresponding to the SEF process. Contrary, when a positive bias is applied, the oxygen vacancies move to the FTO film layer under the action of the electric field, leading to the CF to break at the weakest point, and the device state returns to the HRS, which is called RESET process. Due to the high voltage required by the device RS process, the device is more prone to heat on voltage cycle process. What makes oxygen vacancy permeate into the Au and FTO layer, leading to the redistribution of oxygen vacancy in the device under the action of joule heat. Therefore, after certain cycles of the device, there are not enough oxygen vacancy to form conductive filaments. The device displays the memoryless state, corresponded to the I–V curve in Figure 2(b).

By observing the I–V curve of the analog RS behavior, it could be found that the typical diode rectification effect is accompanied by the RS behavior. In addition, there is an obvious Negative differential resistance (NDR) behavior in the negative bias region, as shown in the inset of Figure 2(c and d). It is generally believed that the causes of such rectification effect is mainly the migration of oxygen vacancies, ferroelectric polarization turnover and interface Schottky barrier [8,27,28]. In order to further verify the mechanism of such rectification effect, we first tested the ferroelectric properties of the samples, the result is shown in Figure 4. The P–V loop of the BFCO thin films at a maximum voltage of 6 V shows unsaturated hysteresis. Which is far less than the previously reported polarization intensity. This can be attributed to the film’s polycrystalline growth, And the surface leakage current is large. This result indicates that ferroelectric polarization does not play a leading role in thin film diode effects. So the diode effect of the thin film can be attributed to the Schottky barrier between Au/BFCO. However, the Schottky barrier model cannot explain the NDR behavior of the thin film.

As discussed above, we established an interface state model to explain the RS behavior with the diode rectification and NDR effect. Because of the oxygen vacancies are always in the perovskite oxide, BFCO thin film can be regarded as an n-type semiconductor, its Fermi level is close to the conduction band. Au and
BFCO. In contrast, an anti-blocking layer with a downwardly band bend is formed on the surface of the BFCO/FTO to accelerate carrier drift and diffusion. As shown in the Figure 5. The red solid circle and the hollow circle represent the interface state occupied by electrons and the non-occupied state, the red arrow represents the process of capturing and releasing electrons, and the black arrow represents the process of electrons crossing the Schottky barrier. When a negative bias voltage is applied to device, that is, the 1,2 process in Figure 2. Because of the acceptor interface state energy level is occupied by the electrons during the continuous cyclic voltage scan, the trapped electrons at the interface state are easily excited to the conduction band than the electrons in metal, so the electrons trapped at the interface state are gradually released as the voltage increases and the current increases with the voltage. The device is in LRS. But as the state trapped electrons gradually decrease, the current gradually decreases after a maximum current appears, showing a NDR effect. After the interface state capture electrons are completely released, the electrons from the Au electrode to the semiconductor conduction band need to cross the Schottky barrier, which is the reason for the rectification effect of the device and the device is in a HRS. Conversely, when a forward bias voltage is applied to the device, the electrons flow from the semiconductor conduction band to the Au electrode, which will first be captured by the interface state, thus the Fermi level move up and the rectification effect will be weakened. The device from the HRS to the LRS, corresponding to the process in Figure 5. Therefore, the second type of RS behavior (analog) can be summarized as a combination of the Schottky barrier and the interface state at the interface. Unlike the first type of RS behavior (digital),
they can all be attributed to the interface-limited conductance behavior.

4. Conclusion
In summary, applying continuous cyclic voltage to the Au/BFCO/FTO/Glass devices can make them exhibit two different RS behaviors. At the beginning, due to the enough oxygen vacancies in the device, the directional movement of the oxygen vacancies under the electric field cause the formation or fracture of the conductive filaments to cause the digital resistive behavior. Meanwhile, the leakage current of the device is large, and the influence of ferroelectric inversion on resistance is covered. As the number of cycles increase, the oxygen vacancies are redistributed under the action of an external electric field, and when the oxygen vacancies in the film are not sufficient to support the formation of oxygen vacant conductive filaments, the device will lose its first type RS behavior. But with the decrease of oxygen vacancies, the leakage current of the device is gradually reduced, and the contribution of the interface effect to the resistance change behavior gradually appears. Therefore, the device exhibits analog RS behavior. So, adjusting the concentration of oxygen vacancies can become an important factor in regulating the mutual switching of digital resistive switching behavior and analog resistive switching behavior of the device. This research provides basis and ideas for designing and manufacturing multifunctional, digital-to-analog conversion resistive memory devices.

Supplementary materials shown the stability characteristics of the two types resistive switching behaviors.

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