# **Resistive Switching in NiO/BiFeO<sub>3</sub> Thin Film**

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**Abstract.** NiO/BiFeO<sub>3</sub> thin film has been deposited on Pt/Ti/SiO<sub>2</sub>/Si substrate by sol-gel method. The structure of thin film is analyzed by X-ray diffraction, and the result of X-ray diffraction shows that a perovskite crystal structure can be well-grown on Pt/Ti/SiO<sub>2</sub>/Si substrate. In addition, the surface morphology is characterized by a scanning probe microscope, and the image of scanning probe microscope indicates a good crystalline quality of NiO/BFO thin film. Moreover, the current-voltage properties are also measured by a semiconductor characterization system, and the stable and reproducible nonvolatile resistive switching characteristic for the memory application have been clearly observed in Pt/NiO/BiFeO<sub>3</sub>/Pt structure, which could be attributed to the formation and rupture of filament localized in NiO thin layer.

# Introduction

Recently, resistive random access memory (RRAM), which is considered as one of the most competitive candidates for next-generation nonvolatile memories, has attracted a tremendous flurry of research interest [1, 2]. On account of this promise, a variety of resistance-switch materials have been extensively investigated. As the most important multiferroic material, multiferroic bismuth ferrite (BFO) is also reported to show the superior resistive switching (RS) characteristics for the fascinating potential application of RRAM [3-5].

Considering the development of BFO applications in practical devices, several problems need to be elucidated. One of the major issues is to concern on the stability of RS characteristics, such as current-voltage cycles, switching voltages, and the resistances of high resistive state (HRS) and low resistive state (LRS). In fact, the instability of RS characteristic would cause several problems in controlling and reading the memory switching states. In order to stabilize the RS characteristics, as well as the memory performance, the method using different material stacks has been studied [6-8]. Kwon et al. [6] observed an improvement of resistive switching characteristics by inserting a thin AlN layer between SiO<sub>x</sub>N<sub>y</sub> layer and the substrate. Pei et al. [7] also found that the resistive switching performance of amorphous indium–gallium–zinc oxide (a-IGZO) RRAM was improved by inserting a thin silicon oxide layer between silver (Ag) top electrode and a-IGZO resistive switching layer. Chen et al. [8] deposited the amorphous MgZnO/ZnO heterostructure films on Pt substrates, and reported that the bipolar resistive switching performances of these structures can be greatly stabilized, and the dispersion of switching voltages and resistance states were suppressed simultaneously. In this work, Pt/NiO/BFO/Pt structures were prepared by sol-gel method, and the reproducible RS characteristics have been investigated in detail.

# Experimental

**Materials.** 1) 99%  $Bi(NO_3)_3 \cdot 5H_2O$  and 99%  $Fe(NO_3)_3 \cdot 9H_2O$  were used to prepare the BFO precursor solution with concentration of 0.2 mol/L. 2) 99%  $NiC_4H_6O_4 \cdot 4H_2O$  was used to prepare the NiO precursor solution with concentration of 0.4 mol/L.

**Methods.** NiO/BFO thin film was fabricated by chemical solution deposition on Pt/Ti/SiO<sub>2</sub>/Si substrate. All the solutions were spin-coated and dried under the same conditions, and finally annealed in air at 550 °C for 30 min. Details on thin film deposition setup were described in the previous study [9, 10]. The structure of film was analyzed by X-ray diffraction (XRD, D-MAX

2200VPC), and the surface morphology was characterized using a scanning probe microscope (SPM, CSPM5500). After Pt top electrodes with a diameter of 0.3 mm deposited on the film surfaces by sputtering, the current-voltage curves were measured by a semiconductor characterization system (SCS, Keithley 4200). The schematic structure of memory cell can be shown in the inset of Fig. 1(a).

#### **Results and Discussion**

The XRD patterns for NiO/BFO thin film deposited on Pt substrate are shown Fig. 1(a). All of the diffraction peaks demonstrate the perovskite crystal structure of BFO, and no impurity phase can be observed, indicating that the thin NiO layer has little effect on the BFO structure. Fig. 1(b) shows the corresponding surface morphology in the SPM image with a scanning area of  $1.78 \times 1.78 \,\mu\text{m}^2$ , and a good crystalline quality can be observed in the NiO/BFO thin film, suggesting that the thin film is well-grown on Pt substrate.



Fig. 1 (a) XRD patterns and (b) SPM image of NiO/BFO thin films.

The nonvolatile RS characteristic of Pt/NiO/BFO/Pt memory cell has been demonstrated in Fig.2(a), where the arrows show the direction of sweeping voltage. To activate the memory cell, a forming process is necessary by applying a high positive voltage of 11 V and a compliance current (CC) of 50  $\mu$ A, which is shown in the inset of Fig. 2(a). After that, the current-voltage properties of RS have been measured for 57 switching cycles. When the positive voltage increases, the current increases suddenly at a set voltage and the memory cell switches from HRS to LRS. However, when a negative voltage is applied, the current drops to a low value rapidly at a reset voltage, and the memory cell switches back to HRS. As can be seen, in Pt/NiO/BFO/Pt memory cell, the set

voltage is distributed from 0.8 to 1.2 V, while the reset voltage is from -0.4 to -0.7 V. Moreover, the resistance evolution of HRS and LRS has also been demonstrated in Fig. 2(b). The resistance ratio is about one order of magnitude with large-resistance dispersion due to the formation and rupture of random and localized conductive filament [10], and it shows no significant degradation of resistance, indicating stable and reproducible RS characteristics for the memory application.



Fig. 2 Resistive Switching characteristics in Pt/NiO/BFO/Pt memory cell.
(a) Current-voltage curves. The inset shows the forming process.
(b) Resistance evolution of HRS and LRS with switching cycles at a read voltage of 0.1V.

Compared to the RS properties of Pt/BFO/Pt memory cell reported in the previous study [11], it can be clearly observed that current-voltage curves with successive switching cycles can be greatly stabilized not only in Pt/BFO/NiO/Pt memory cell but also in Pt/NiO/BFO/Pt memory cell. On the basis of these results, the sketches of RS mechanism are depicted in Fig. 3. In general, from the view of conductive filament [10], the ionized oxygen vacancies (OVs) in the thin film can migrate from the anode to the cathode and capture the free electrons to become neutral, and then these neutralized OVs are connecting and forming a conductive filament, which needs a quite high voltage. Once the conductive filament is accomplished, the formation and rupture of filament could be random and localized. However, in Pt/NiO/BFO/Pt memory cell, owing to the lower activation energy and the high conductivity of OV in NiO materials, the formation and rupture of filament may easily take place at the NiO thin layer, which can confine filamentary conducting path locally much better, avoiding their random formation and rupture, giving the stable resistive switching. It is worth mentioning that, compared to Pt/BFO/NiO/Pt memory cell, the threshold RS property cannot be observed in Pt/NiO/BFO/Pt memory cell, probably due to the thermal dissipation process easily occurred on the NiO surface, which retain the film temperature below the critical value and prevent the memory RS converting to the threshold RS [11].



Fig. 3 Sketches of resistive switching mechanism in Pt/NiO/BFO/Pt memory cell.

### **Summary**

NiO/BFO thin film has been fabricated by chemical solution deposition on Pt/Ti/SiO<sub>2</sub>/Si substrate, and the analysis of the structure and the surface morphology demonstrates a good crystalline quality of thin film. Moreover, according to the measurement of current-voltage properties, the stable and reproducible nonvolatile resistive switching behavior has also been investigated in Pt/NiO/BFO/Pt memory cell, which can be attributed to the formation and rupture of filament well localized in NiO thin layer, indicating that a multifunctional memory application would be feasible.

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