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Citation: *Applied Physics Letters* **97**, 042101 (2010); doi: 10.1063/1.3467838

View online: <http://dx.doi.org/10.1063/1.3467838>

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## Resistance switching in polycrystalline BiFeO<sub>3</sub> thin films

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(Received 17 May 2010; accepted 27 June 2010; published online 26 July 2010)

We report resistance switching effects in polycrystalline pure BiFeO<sub>3</sub> films prepared by a sol-gel method. By current-voltage and conductive atomic force microscope (c-AFM) measurements, resistance switching effects are observed in BiFeO<sub>3</sub> films annealed at and above 650 °C. A fresh sample can be transformed into a low-resistive state by applying a high positive voltage without forming process and then be switched to a high-resistive state by applying a negative voltage. Both c-AFM and retention results suggest that the redistribution of oxygen vacancies in grain boundaries could play a key role on the resistance switching in the polycrystalline pure BiFeO<sub>3</sub> films. © 2010 American Institute of Physics. [doi:10.1063/1.3467838]

Bismuth ferrite BiFeO<sub>3</sub> (BFO) has attracted much attention as a multiferroic material in which ferroelectric and antiferromagnetic ordering temperatures are both above room temperature.<sup>1–4</sup> However, a large leakage current often occurs in BFO thin films due to the presence of oxygen vacancies created in the film growth process, which makes BFO films difficult to be polarized to the saturation and hinders their applications as a ferroelectric material.<sup>5</sup> Several methods have been used to reduce the leakage current, such as annealing BFO thin films in oxygen and doping BFO with higher valence ions.<sup>6</sup> On the other hand, the leakage current in BFO can be used to some extent in some applications,<sup>7,8</sup> for example, in nonvolatile resistive random access memory. It was thought that the magnetoelectrics and magnetoelectronics at room temperature can be merged by combining electronic conduction with electric and magnetic degrees of freedom in the multiferroic BFO.<sup>9</sup> A reversible modulation of electric conduction has been found in Ca-doped BFO epitaxial films.<sup>9</sup> However, no resistance switching behaviors have been reported in polycrystalline BFO thin films so far. Due to the presence of grain boundary defects in polycrystalline thin films, the electric conduction behaviors in polycrystalline films might be different from those in epitaxial films.

In this paper, we report the resistance switching behaviors in pure BFO polycrystalline films fabricated by a sol-gel method. It is found that the current-voltage (*I-V*) curves of polycrystalline BFO films show a large difference with those of epitaxial Ca-doped BFO films. The redistribution of oxygen vacancies in grain boundaries is thought to play a key role on the resistance switching behavior.

The BFO thin films were fabricated by a sol-gel method on commercial Pt/Ti/SiO<sub>2</sub>/Si (111) substrates, followed by post annealing at temperatures from 450 to 700 °C in air. Cross-section transmission electron microscopy [TEM (Tecnai G<sup>2</sup> F20, FEI)] was employed to examine the microstruc-

ture. The atomic force microscopy [AFM (Dimension V, Veeco)] was used to detect the surface morphology and leakage current [conductive-AFM (c-AFM) mode]. In order to measure the electrical properties of the BFO films, Cu top electrode pads with a thickness of 200 nm and a diameter of 100 μm were deposited onto the BFO films by electron-beam evaporation. The *I-V* characteristics of Cu/BFO/Pt sandwich structures were studied by means of Keithley 4200 Semiconductor Characterization Systems with the Cu top electrodes being grounded. In the local leakage current measurement by c-AFM, the conductive tip was grounded and directly touched the BFO films.

The *I-V* cycle of a fresh sample annealed under 700 °C was plotted in Fig. 1(a). The bias voltage was swept as 0 V → 3 V → 0 V → -3 V → 0 V. It can be seen that the *I-V* curve shows a symmetric feature rather than a rectifying one, which was reported in epitaxial Ca-doped BFO films.<sup>9</sup> The current increases sharply at about 2.7 V in the positive bias region and the sample changes from the high resistance state (HRS) to a low resistance state (LRS). The sample holds on the LRS until the voltage is decreased to about -2.7 V, where a negative differential resistance appears. As shown in Fig. 1(b), c-AFM measurements in which the AFM tip is in perpetual contact with the sample also demonstrate similar symmetric *I-V* characteristics though the threshold voltages are higher (±7.5 V) probably due to the nonideal contact between the AFM probe and BFO films as well as very small contact area compared to the conventional *I-V* characterization. Both the *I-V* and c-AFM results are well reproducible for the identical voltage sweeps.

Typical c-AFM measurements were also performed in the same region of 2 × 2 μm<sup>2</sup> in size under various dc voltages, as shown in Fig. 1(c). No obvious leakage current is detected under a read voltage of 3 V for a fresh sample. After applying a large write voltage of 10 V, the leakage currents in some regions reach ~50 pA under a read voltage of 3 V. As an erase voltage of -5 V is applied, the leakage current

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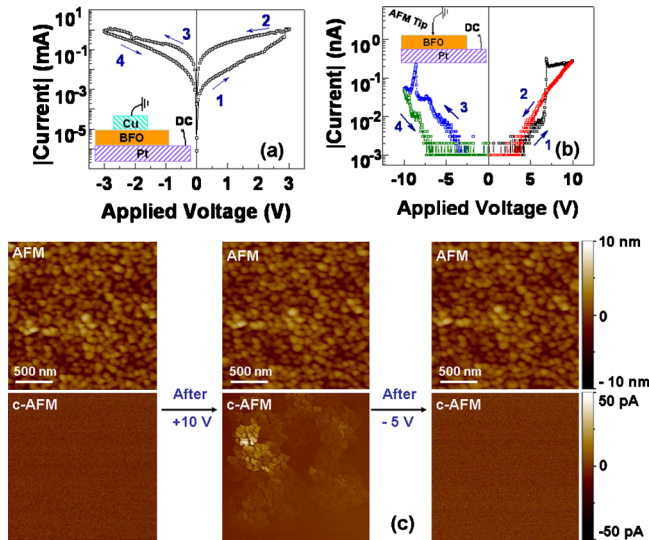


FIG. 1. (Color online) (a) The resistance switching behavior of the BFO film annealed at 700 °C with a conventional sandwiched structure as shown in the inset. (b) Local  $I$ - $V$  measurement in which the AFM tip is in perpetual contact with the sample. (c) AFM and corresponding c-AFM images under the read voltage of 3 V with a scanning size of  $2 \times 2 \mu\text{m}^2$ .

vanishes again under 3 V. These c-AFM measurement results indicate clearly the resistance switching effect in BFO polycrystalline films.

Although the sol-gel method has been widely used to prepare BFO thin films, no resistance switching behaviors have been reported so far in this system. Notably, most of these BFO films were prepared with post annealing temperatures lower than 650 °C.<sup>10,11</sup> To demonstrate the influence of annealing temperature on the resistive switching of BFO films,  $I$ - $V$  measurements and cross-section TEM analyses were performed. The  $I$ - $V$  characteristics of the samples with various annealing temperatures are shown in Fig. 2(a). The bias voltage is swept as 0 V  $\rightarrow$  3 V  $\rightarrow$  0 V. No hysteretic  $I$ - $V$  characteristics are found in the samples annealed below 650 °C, while an obvious  $I$ - $V$  hysteresis is observed in the

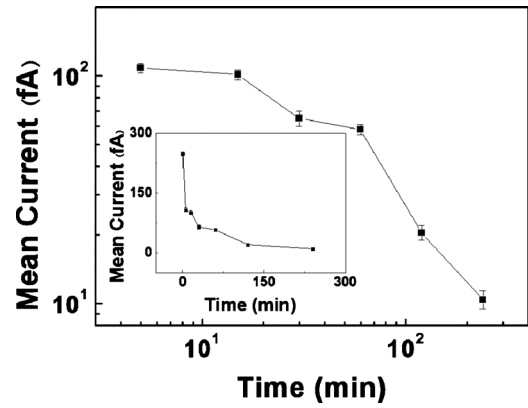


FIG. 3. Mean tip current in a selected area as a function of retention time. The inset shows the same curve in linear scale.

samples annealed at and above 650 °C. The average grain size of the samples annealed at 700 °C is much larger than that of the samples annealed at lower temperatures, as shown in Figs. 2(b)–2(d). From Fig. 2(a), it can be seen that the leakage current increases with annealing temperature. Since oxygen vacancies play a key role on the leakage current in BFO systems,<sup>6,12</sup> we deduce that the oxygen vacancy concentration increases with annealing temperature. Similar to epitaxial Ca-doped BFO films,<sup>9</sup> one can conclude that the proper oxygen vacancy concentration plays an important role on the resistance switching behaviors of polycrystalline BFO thin films.

The retention experiment was also conducted by means of c-AFM. After applying a write voltage of 10 V, a read voltage of 3 V was employed to probe the resistance state at various intervals. Figure 3 shows the mean tip current (the mean leakage current in a given region of BFO films) as a function of the retention time within a selected area. As shown in Fig. 1(c), the conduction is not uniform in the scanned region. Some areas are in the LRS while others remain in the HRS, which leads to the low mean tip current. From Fig. 3, one can see that the LRS can last several tens of minutes and then decays gradually. This conduction decay can be attributed to the oxygen vacancy migration.<sup>9</sup> The oxygen vacancy diffusion length can be evaluated using the following equation:<sup>9</sup>

$$L^2 = 4Dt, \quad (1)$$

where  $L$  is the diffusion length,  $D$  is the diffusivity of oxygen vacancies, and  $t$  is the diffusion time. The diffusivity of oxygen vacancies is about  $10^{-17} \text{ cm}^2 \text{ s}^{-1}$ .<sup>9</sup> The diffusion time can be determined roughly as 50 min from Fig. 3. Then the oxygen vacancy diffusion length  $L$  in our samples can be calculated to be about 3.5 nm. The diffusion length is much less than the thickness of BFO films while is close to the width of grain boundaries. Therefore, the p-n junction mechanism proposed in epitaxial Ca-doped BFO thin films could not be available in the polycrystalline BFO films due to the short diffusion length of oxygen vacancies.

A simple model is proposed below to explain the observed resistance switching behaviors. As reported by Guo *et al.*,<sup>13</sup> the distribution of oxygen vacancies in grain boundaries is different from that in grain interiors due to the defect structure. A fresh polycrystalline BFO film is most likely to be in an HRS considering the large grain boundary

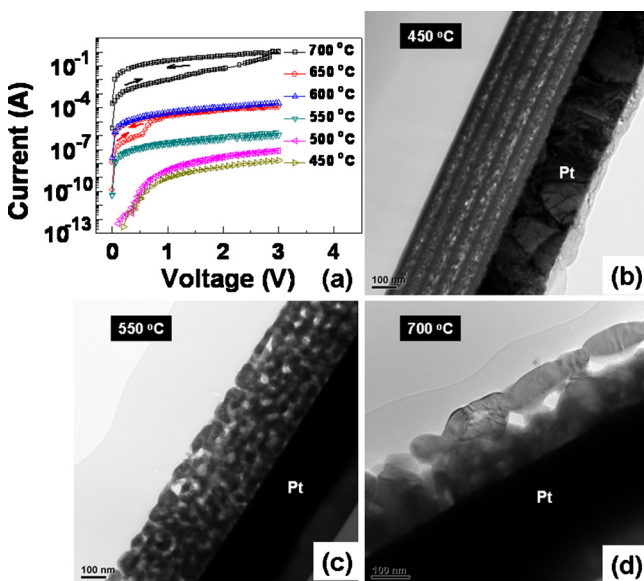


FIG. 2. (Color online) (a)  $I$ - $V$  characteristics of BFO thin films annealed at various temperatures. Cross-section TEM images of BFO films annealed at (b) 450 °C (c) 550 °C, and (d) 700 °C, respectively.

resistances.<sup>13</sup> When a high bias voltage is applied, oxygen vacancies redistribute under the high electrical field and conduction paths might be formed across grain boundaries, thus the sample switches to the LRS. After a certain negative bias voltage is applied, the redistributed oxygen vacancies are recovered and the conductive channels are destroyed, then the sample returns to the HRS. No other phases are detected by both x-ray diffraction and high-resolution TEM. As a result, the effect of other phases is not regarded in this scenario.

In conclusion, the electric transport properties of polycrystalline BFO films prepared by a sol-gel method have been investigated by means of *I-V* and c-AFM measurements. The resistance switching behaviors without the forming process are found in the BFO films annealed at and above 650 °C. The c-AFM and retention measurements suggest that the redistribution of oxygen vacancies in grain boundaries under an electric field plays a key role on the resistance switching behaviors.

The authors thank Dr. Jinzhi Wang and Gongcheng Zhou for their valuable discussion. The authors acknowledge the financial support from Chinese Academy of Sciences, National Natural Science Foundation of China, State Key Project of Fundamental Research of China (973 Program), Zhejiang, and Ningbo Natural Science Foundations.

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