Electric field-induced resistance switching in $(Bi_2O_3)_{0.7}(Y_2O_3)_{0.3}$ films

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Single-phase $(Bi_2O_3)_{0.7}(Y_2O_3)_{0.3}$ (BYO) films are obtained by pulse laser deposition under the temperatures from 300 to 500 °C and the oxygen pressure of 90 Pa. Electric field-induced resistance switching is observed in the Ag/BYO/Pt structure. Postannealing in 750 °C improves the repeatability of the resistance switching and narrows the distribution of the set and reset voltages triggering the resistance switching. A linear variation of reset current with resistance is obtained for the Ag/BYO/Pt systems, either as-prepared or postannealed, despite the great dispersion of these two quantities. A reduction in the activation energy, from ~0.63 to ~0.33 eV, for the migration of oxygen vacancies is observed after the forming process. Possible mechanisms are discussed. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3106660]

I. INTRODUCTION

While traditional memories are approaching their scaling limits, the information industry needs to develop smaller, faster, and cheaper memory device working based on new principle, new materials, and new structures. It has been found that the resistance of electrode/oxide/electrode system can experience a great change under the impact of electric pulses, and the resulting resistance state can retain for days, even months, without significant decaying.[1] This effect has attracted great attention due to its potential application to information storage. A model of resistance random access memory (RRAM) has been proposed based on this effect, which is believed as one of the most promising candidates for information storage because of its superior characteristics such as simple structure, high integration density, low power consumption, fast read/write speed, and compatibility with current semiconductor technology. Although resistance switching has been observed in many kinds of materials, such as the binary oxides TiO_2, NiO, Fe_3O_4, CoO, Cu_2O, ZnO, and ZrO_2,[2–8] the perovskite oxides Cr and La doped $SrTiO_3$, $Pr_{0.7}Ca_{0.3}MnO_3$, and $La_{0.7}Ca_{0.3}MnO_3$,[9–12] and the solid electrolytes Cu_2S, Ag_2S, Ta_2O_5, Cu doped SiO_2, WO_3, $Ge_{0.3}Se_{0.7}$, RuAgI,[13–19] the exploration for new materials that have the property of easy preparation and excellent performance is still under way.

Up to now, the exact mechanism for the resistance switching has not been well understood, although various models have been proposed, such as the formation and rupture of metallic filaments,[20] variations of Schottky barriers,[21] and the trap charging/discharging process.[22] With the use of any switching models, the defects in materials will play a critical role in the resistance switching. For the transitional oxide materials, indeed, it has been demonstrated that the resistance switching can be caused by the oxygen vacancy rearrangement.[23] Bi_2O_3 ceramic is a typical oxygen ionic conductor, which generally have high oxygen vacancy mobility at high temperature (above 700 °C). By doping with rare earth ions, the oxygen vacancy mobility near the ambient temperature can be enhanced.[24] It is easy to understand that, if oxygen vacancy migration is responsible for the field-induced resistance change, this material may show the resistance switching properties. Considering the fact that studies on this material are still lacking, in this paper, we will report a comprehensive study on the resistive switching in $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ (BYO) films. Unipolar resistance switching behavior is observed in the BYO films. Key factors that influence the resistance switching effect, such as the homogeneity of the films, the mobility of oxygen vacancies, and the activation energy for oxygen migration, are studied and the possible mechanisms are discussed.

II. EXPERIMENTS

$(Bi_2O_3)_{0.7}(Y_2O_3)_{0.3}$ ceramic target was prepared using the solid-state-reaction technique. The mixture of Bi_2O_3 (99.9%) and Y_2O_3 (99.9%) powders with stoichiometric proportion was first thoroughly grinded in agate mortar then sintered at 800 °C for 5 h. After a regrinding, the product was pressed into pellets under the pressure of ~30 MPa, and sintered again at 800 °C for 5 h. BYO films were deposited on commercial $Pt/Ti/SiO_2/Si$ substrates using the pulsed laser ablation technique. To explore the effect of preparation condition, the deposition temperature was changed from ~300 to ~750 °C and the oxygen pressure from ~10 to ~100 Pa. Ag electrode matrixes were deposited on the sample through a shadow mask, and the size of each electrode is ϕ0.4 mm in diameter.

A Rigaku x-ray diffractometer was used for the characterization of the samples. Surface morphology of the films was studied by a scanning electron microscopy (SEM). Current (I)-voltage (V) characteristics were measured by the two-probe technique, using a Keithley SourceMeter 2400 controlled by computer. Positive bias is defined as the one from Ag to Pt. A current compliance of 10 mA was set to protect the samples from electric breakdown.

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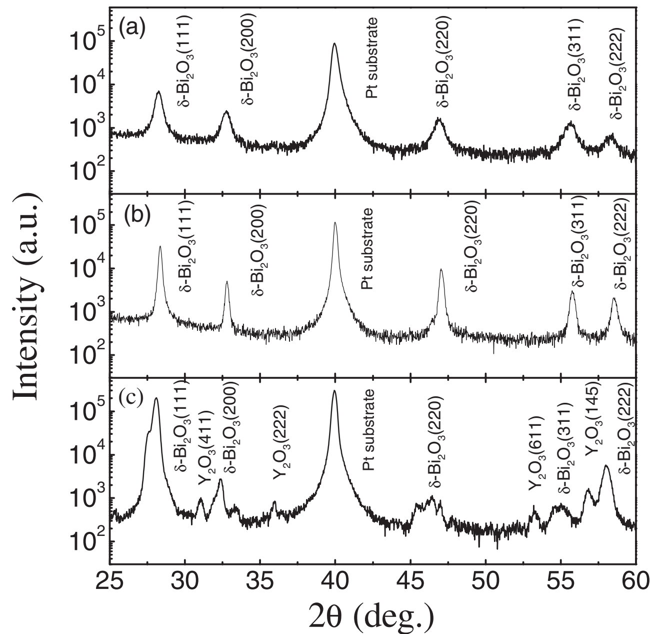

FIG. 1. XRD patterns of (a) BYO-1, (b) BYO-2, and (c) BYO-3, prepared, respectively, under the temperature of 300, 500, and 500 °C plus a postannealed at 750 °C for 10 min. Y_2O_3 phases appear after postannealing.

III. RESULTS AND DISCUSSIONS

Figure 1 present the x-ray diffraction (XRD) pattern of the BYO films prepared under different temperatures. The films grown under the temperatures of 300 and 500 °C, denoted as BYO-1 and BYO-2, respectively, exhibit the structure of δ-Bi_2O_3 (Ref. 24) without secondary phases. XRD peaks of different crystal planes are observed, which indicate the polycrystalline character of the samples. There are no preferred orientations compared with the standard XRD pattern of bulk BYO. Only the films deposited at the temperatures below 700 °C and the oxygen pressure above 60 Pa well crystallized in the δ-Bi_2O_3 structure. Postannealing affects the texture of the film, as demonstrated by the visible growth of the (111) peak of the BYO-2 film postannealed at 700 °C for 10 min in an oxygen pressure of 90 Pa (labeled as BYO-3 hereafter) [Fig. 1(c)]. Considerable impurity phases (Y_2O_3) appear after the heat treatment, which could be a consequence of the evaporation of Bi in the films. Figure 2 shows the SEM images of BYO-2 and BYO-3. It is obvious that the postannealing leads to coarser grains and larger apertures between grains.

As occurred in other oxides, to activate the unipolar switching properties of the BYO films, a forming process that completes under a much high voltage is required. The maximum voltage required here is ~6 V, which triggers a high to low resistance switching of the sample (not shown). Figure 3 shows the typical *I-V* characteristics of BYO-3 after the forming process, obtained by repeating the measurements 40 times. The current rapidly increases at a critical voltage V_{set}, which fluctuates between ~1.1 and ~1.4 V, signifying a high to low resistance switching. The sample stays in the low resistance state (LRS) while releasing the electric stress to 0, and a sudden current drop that manifests the backward switching appears after the bias exceeds $V_{reset} \approx 1$ V during

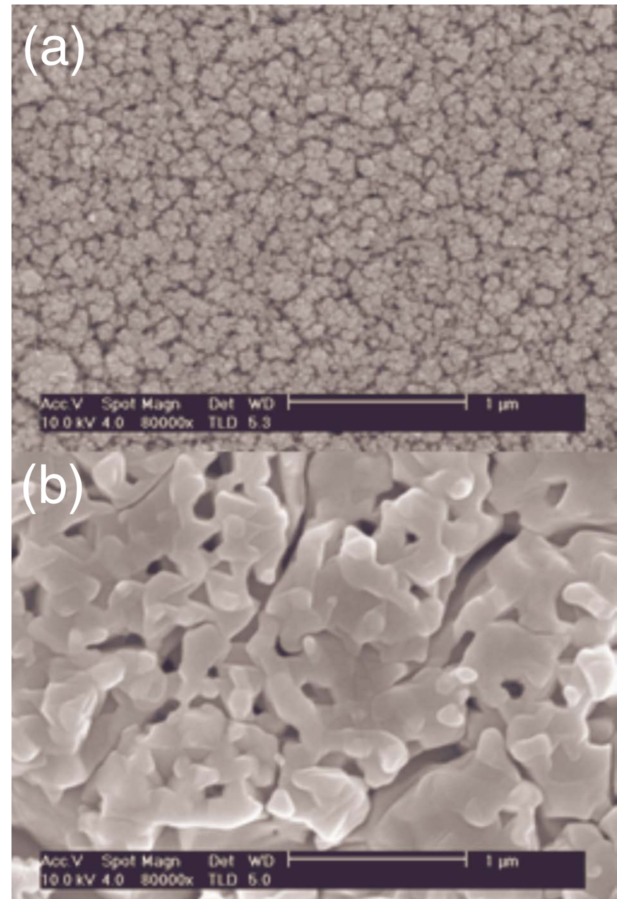

FIG. 2. (Color online) SEM images of BYO-2 (a) and BYO-3 (b). Significant grain growth occurs in the latter sample.

the subsequent application of electric field. Although there is a significant fluctuation in critical voltages, which reflect the inhomogeneity of the films, the relation $V_{set} > V_{reset}$, is always true. The difference between V_{set} and V_{reset} provides an operation window between two states, which is important to practical application. These phenomena are similar to those observed in other oxides of different structures, and are general features of the resistance switching.

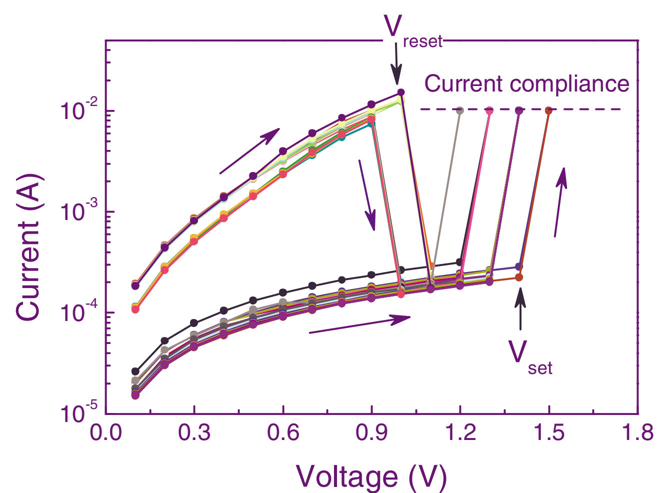

FIG. 3. (Color online) Current-voltage characteristics of BYO-3 after the electric forming process.

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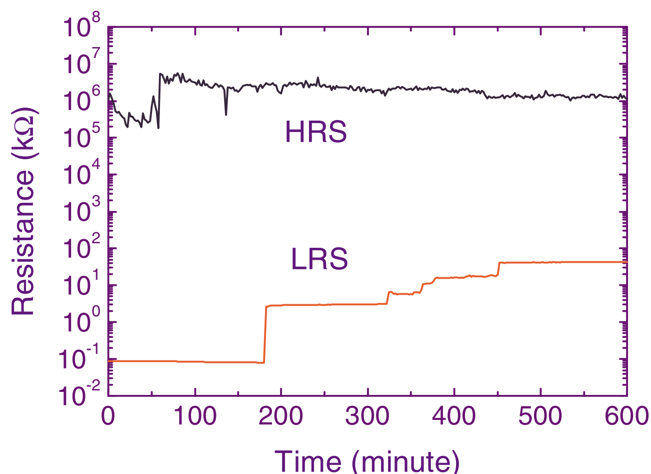

FIG. 4. (Color online) Relaxation of the resistance of the HRS and the LRS for sample BYO-2.

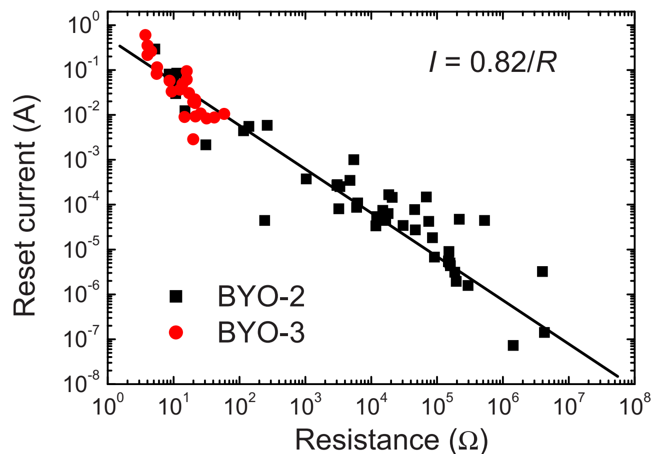

FIG. 5. (Color online) Reset current as a function of resistance for the Ag/BYO/Pt structure. Data represented by different symbols are extracted from the *I-V* characteristics obtained by repeated measurements under both the positive and negative biases. Solid line is a guide for the eye.

Resistance switching is also observed in BYO-2 (not shown). Although the high-to-low resistance ratio in this film is much greater compared with BYO-3, both the resistance, either in the LRS or in the high resistance state (HRS), and the critical voltages disperse in a wide range. This result reveals the great inhomogeneity of the sample. In contrast, no stable resistance switching is observed in BYO-1. The low growth temperature can affect the crystallinity of the sample, which may be the reason for the instability.

The resistance of BYO-3 is stable, both in the LRS and in the HRS. Considerable relaxation is observed in BYO-2. As shown in Fig. 4, the HRS is quite stable, and its resistance retains for ~10 h without considerable decaying. In contrast, the resistance of the LRS exhibits stepwise relaxation, and the maximum resistance change is nearly three orders in magnitude. Fortunately, the resistance relaxation, though it is great, is far from blurring the resistance difference of the HRS and LRS.

The mechanism for the resistance switching in the metal-oxide system is still not clear at present. A prevalent explanation is the formation/rupture of conduction filaments in the insulating oxides, under the impact of electric pulses. According to this model, tiny conducting pathways formed by aligned defects in the HRS can grow or merge with each other, under the driving of electric pulses, forming coarse conducting channels. This is the reason for the occurrence of the HRS to LRS transition. However, the conducting filaments can be molten by the large current through them when the electric pulses are reapplied,[25] and the backward LRS to HRS switching occurs. In this scenario, the current that leads to the resistance switching may have a close relation to the resistance of the systems. In Fig. 5 we show the dependence of reset current on resistance obtained for different samples. The data represented by different symbols are extracted from different *I-V* characteristics obtained from repeated measurements under both the positive and negative biases. A monotonic increase in reset current with device resistance is observed. The former is, respectively, ~1.6 μA and ~0.3 A when the resistance takes the values of $\sim 3\times 10^5$ Ω and ~5 Ω. A further analysis reveals the presence of a simple relation $I \approx 0.82/R$. It means that the average reset voltage would be ~0.82 V, and the changes in reset current originate from the variation of device resistance. This result is important in the sense that it indicates the presence of a general rule for the BYO films, either as-prepared or postannealed, though the resistance switching behavior, especially for BYO-2, is apparently random.

As revealed by various experiments, pretreatments by high electric fields, namely, the forming process, are necessary for the resistance switching of the systems. It is this process that activates the oxygen vacancies, making their migration feasible. It may be instructive to check the variation in the activation energy of oxygen vacancies before and after the forming process. As well established, the ionic mobility of solid electrolytes can be described by $\mu \propto a^2 v \exp(-\varepsilon_a/k_B T)/T$, where a is the interatomic distance, v is the frequency characterizing the lattice vibration, and ε_a is the activation of ionic diffusion. From the relation $\mu \propto I$, the ionic mobility of the samples can be deduced from the current recorded under different temperatures at a fixed bias voltage. Figure 6 shows the current of BYO-2 as a function

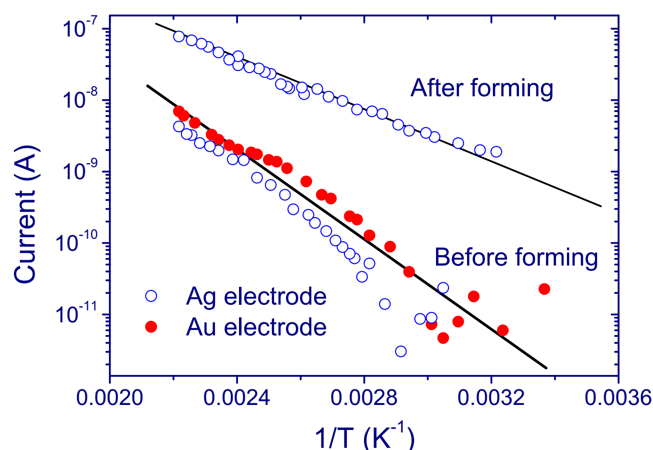

FIG. 6. (Color online) Temperature dependence of the current measured under the bias of 0.1 V for the M/BYO-3/Pt sample (M=Ag and Au) before and after the forming process. Solid lines are guides for the eye.

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of temperature, measured under the bias of 0.1 V. Two kinds of electrodes, Au and Ag, were used in the M/BYO-2/Pt system (M=metal). The temperature interval investigated is from 290 to 450 K. Two $I-1/T$ relations are obtained, measured before and after the forming process, respectively. A well linear dependence between $\ln I$ and $1/T$ is observed, which indicates an exponential decay of current with temperature with a rate characterized by the activation energy of oxygen according to the above equation. A direct calculation gives the activation energy of ~0.63 eV before the forming process. This is a value smaller than that in the bulk BYO, which is ~1 eV below 500 °C. This could be due to the higher vacancy density in the films compared with bulk materials. Electric forming causes a significant reduction in activation energy, and a value of ~0.33 eV, nearly half that in the as-annealed sample, is obtained. We found that the forming process proceeds only in the sample with the Ag electrode, and it cannot be completed in the Au-BYO interface even when a hard electric breakdown occurs above the applied voltage of 20 V. As a result, only the data of Ag/BYO-2/Pt are presented here after the forming process.

According to previous studies, metallic electrodes are crucially important for resistance switching. Metallic electrodes with the ability absorbing oxygen can extract oxygen from neighboring oxides to form metallic oxides,[26] leaving oxygen vacancies. The electrochemical migration of these vacancies under the driving of electric field yields the dramatic electroresistance effect. The forming process is actually the process for the creation of oxygen vacancies near the Ag-BYO interface. The increase in the density of oxygen vacancies makes it easy for the oxygen to diffuse. This explains the reduction in the activation energy after the forming process. Based on the present results, we can also conclude that Ag is superior to Au in yielding oxygen vacancies in the oxides.

As a supplement, we would like to point out that no special features associated with high oxygen ionic conductivity of BYO are observed in the present work. This may be a hint that the oxygen diffusion proceeds may be mainly through grain boundaries of BYO. As well known, oxygen mobility is much greater near grain boundaries than in grain inner. This result indicates the unimportance of the intrinsic oxygen mobility for the polycrystalline materials.

IV. SUMMARY

BYO films are prepared, using pulsed laser deposition technique, and their electroresistance effect has been experimentally studied. Single-phase BYO films are obtained prepared under the temperatures from 300 to 500 °C and the oxygen pressure of 90 Pa. Electric field-induced resistance switching behavior is observed in the Ag/BYO/Pt structure. Postannealing in 750 °C improves the repeatability of the electroresistance and narrows the distribution of set and reset voltages for the resistance switching. A linear variation in reset current with resistance is obtained for the Ag/BYO/Pt systems either as-prepared or postannealed despite the great dispersion of these two quantities. A reduction in the activation energy, from ~0.63 to ~0.33 eV, for the migration of oxygen vacancies is also observed after the forming process. The occurrence of excessive oxygen vacancies after the forming process is believed to be responsible for this result.

ACKNOWLEDGMENTS

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