

Unipolar Resistive Switching of Eu_xO_y Polycrystalline Films

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Polycrystallized Eu_xO_y thin films show unipolar resistive switching. The ratios of the resistance values of the high-resistance state to those of the low-resistance state are as large as 10^8 . The deposited Eu_xO_y thin films show mixed phases, Eu_2O_3 and Eu_3O_4 . The relative concentration of the phases could be controlled by using the oxygen gas flow rate during growth. A high oxygen concentration leads to broadening the distribution of the switching voltages, inducing transitions between the high-resistance state and the low-resistance state. We observe that the distribution of the switching voltage from the high-resistance state to the low-resistance state (V_{SET}) is smaller than or comparable to that of the switching voltage inducing the opposite transition (V_{RESET}) in well-controlled Eu_xO_y thin films.

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I. INTRODUCTION

Resistive switching, that is, bistable transitions between a high-resistance state and a low-resistance state, has been observed in many metal-insulator-metal layered structures [1]. Bistable resistive switching operations require an external voltage or current with either a polarity reversal or a successive increase. Depending upon the requirement of the polarity reversal, resistive switching is divided into either “bipolar” or “unipolar”. From the memory device point of view, materials with unipolar switching need simpler circuits for memory array operations. Transition-metal oxides, such as NiO and ZrO_2 , are widely studied because they show unipolar switching behaviors and good retention properties for non-volatile memory devices, such as resistive random access memories (RRAMs) [2–7].

There are, however, a few issues to be solved for practical devices using unipolar switching behaviors, such as the leakage current [8] and the distribution of transition voltages [9]. A high leakage current results in high power consumption and rapid temperature increase during device operation. A wide distribution of the transition voltage may bring about writing failure due to reversal of the switching voltages. We report, for the first time, repro-

ducible resistive switching of europium (Eu)-oxide thin films. They show unipolar memory switching behavior with smaller transition voltage distributions than those of transition-metal-oxide films.

II. EXPERIMENTS AND DISCUSSION

Eu_xO_y thin films are grown on Pt/Ti/SiO₂/Si (111) substrate in a radio-frequency magnetron driven sputter modified for the growth of oxide materials. A EuO target, 99.9 % pure, is used during the growth. The base pressure before sputtering is kept below 1.0×10^{-6} Torr by using a turbo-molecular pump. The Eu_xO_y thin films are grown under a gas pressure of 5 mTorr with simultaneous argon and oxygen gas flow. Eu_xO_y film thicknesses are measured by scanning electron microscopy. An approximately 450-nm thickness was obtained at a substrate temperature of 550 °C and an RF power of 300 W for 20 minutes. For the transport measurements, an additional 100-nm-thick top Pt layer is deposited and photo-lithographically patterned. These Pt electrodes have square shapes with various sizes: $100 \times 100 \mu\text{m}^2$, $50 \times 50 \mu\text{m}^2$, etc. In this paper, we present experimental results from two samples grown with different oxygen-gas partial flow rates. Sample A is grown with an oxygen flow of 1 sccm and an argon flow of 39 sccm while sample B is grown with an oxygen flow of 8 sccm and an argon flow of 32 sccm. The resultant partial pressures of oxygen for sample A and sample B are 2.5 % and 20 %, respectively.

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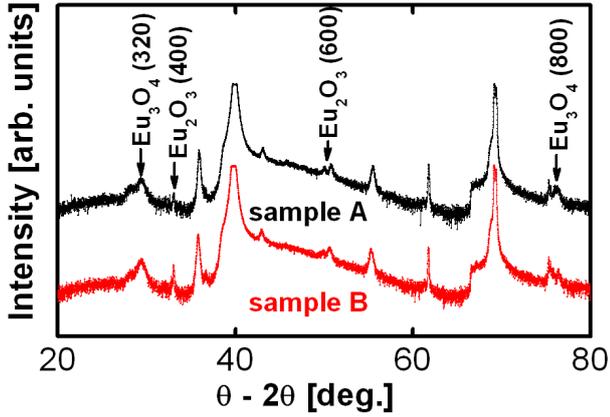


Fig. 1. XRD plot of Eu_xO_y thin films. Sample A and sample B are deposited under a 2.5 % and a 20 % oxygen partial pressure, respectively. Mixed phases of Eu_2O_3 and Eu_3O_4 are identified in the plot.

Table 1. Relative ionic concentrations of Eu_xO_y measured by using XPS.

Material	Oxygen 1s	Eu 4d
Sample A	52.68 %	47.32 %
Sample B	54.45 %	45.55 %

The electric transport properties of the films are characterized by using current-voltage (I - V) measurements. The samples are mounted in a probe station and the top Pt electrode and the bottom Pt layer are connected to a Keithly 2400 general-purpose source meter. The current flow through the film is measured while the external voltage across the film changes at room temperature. The voltage increases in 100-mV steps until the current reaches the pre-set compliance currents. This function allows the measurement system to stop applying voltage when the current flows too much to rupture the samples. During the transition from the high-resistance state to the low-resistance state (SET transition), the compliance current is set as low as possible to 10 μA while repetitive switching persists. For the transition from the low-resistance state to the high-resistance state (RESET transition), the compliance current of 1 A is chosen. We choose the lowest possible compliance currents for the SET and the RESET transitions in order to minimize the effect due to the local Joule-heat generated in the material during the switching operation.

X-ray Diffraction (XRD) measurements were performed to identify the phases of Eu_xO_y . The XRD scanning mode is a theta-2 theta scan from 20 degree to 80 degree. A monochromatic copper- $\text{K}\alpha$ X-ray source at a wavelength of 1.5406 \AA is used. XRD measurements show all films have polycrystalline mixed phases of Eu_2O_3 and Eu_3O_4 , as shown in Figure 1. The peak locations are identified according to the table published by the Joint Committee on Power Diffraction Standards,

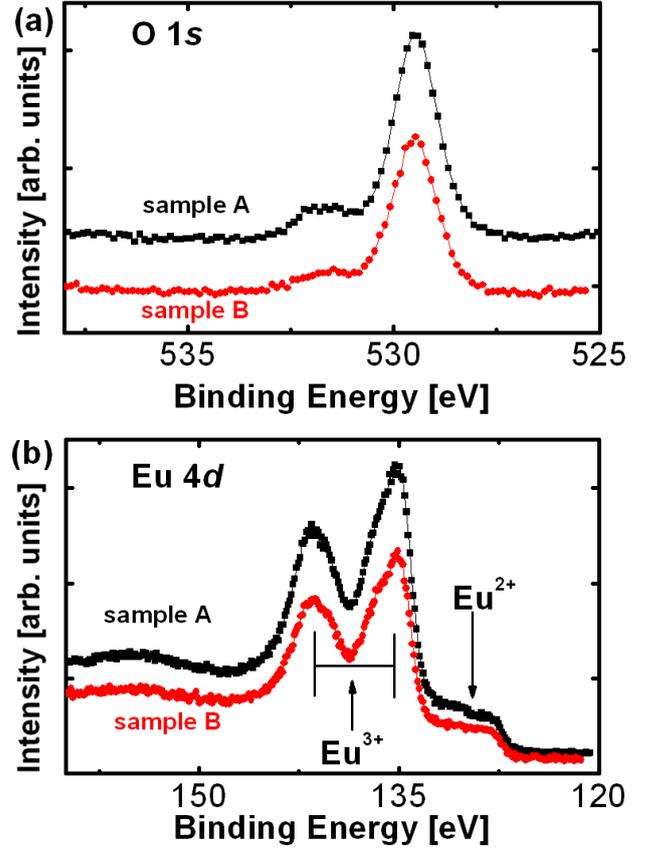


Fig. 2. (a) Oxygen 1s XPS spectra of sample A and sample B deposited under a 2.5 % and a 20 % oxygen partial pressure, respectively. (b) Eu 4d XPS spectra of sample A and sample B.

version 2000. No other phases, such as with higher Eu valences, could be identified. The Eu_2O_3 phase is a stable phase with a Eu valence 3^+ , but the Eu_3O_4 is a multiphase alloy composed of two compounds, EuO (Eu^{2+}) and Eu_2O_3 (Eu^{3+}). No noticeable peak shifts were observed.

In order to find the ionic concentrations of Eu and oxygen, we performed X-ray photoelectron spectroscopy (XPS), as shown in Figure 2. A monochromatic aluminum- $\text{K}\alpha$ X-ray source at 1486.6 eV is used with a beam diameter of 100 μm . The spectral resolution of the instruments is approximately 0.4 eV. Samples are Ar-sputtered *in-situ* for clean surfaces. All XPS measurements are performed in an ultrahigh vacuum chamber operated under 1×10^{-10} Torr at room temperature. The spectra are normalized to the C 1s peak at 285 eV.

Figure 2(a) and (b) show XPS spectra of oxygen 1s and Eu 4d, respectively. The shoulder peak at 533 eV of the oxygen 1s peak at 529 eV is due to surface contamination. Eu 4d spectra show a divalent $4d4f^7$ configuration at 125 eV and a multiplet structure of the trivalent $4d4f^6$ configuration [10]. The peaks are fitted after Lorentzian-Gaussian deconvolution processes. The relative oxygen

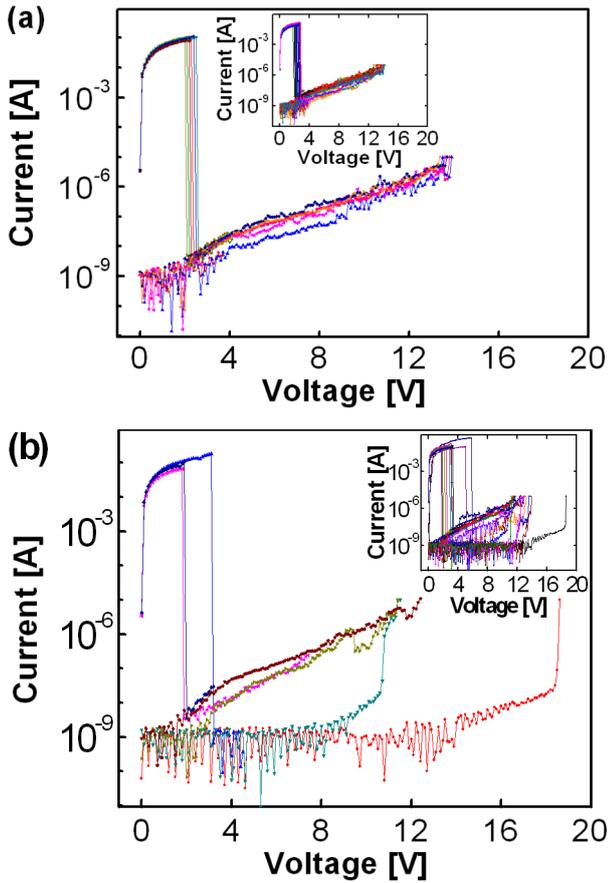


Fig. 3. Typical I - V plots of sample (a) A and (b) B measured with a single $100 \times 100 \mu\text{m}^2$ top electrode. Reproducible resistive switching can be observed. The insets show overlapped plots from many electrodes of $100 \times 100 \mu\text{m}^2$ size patterned on each sample.

ion concentrations and Eu ion concentrations could be determined from the intensities of the fitted peaks and are summarized in Table 1; sample A has a lower oxygen concentration than sample B by 3.25 %.

The I - V measurement data of samples A and B, as shown in Figures 3(a) and 3(b), reveal resistive switching behaviors of the samples under $100 \times 100 \mu\text{m}^2$ electrodes. All samples show reproducible unipolar resistive switching. In order to describe the switching behavior more conveniently, we follow the conventional definitions of terms used in Ref. 2: The SET voltage V_{SET} is defined as the voltage across the SET transition (from the high-resistance state to the low-resistance state). The RESET voltage V_{RESET} can be defined as the reverse. If reproducible resistive switching is to be generated for transition-metal-oxide films, a high voltage needs to be applied from the pristine state. This operation (or transition) is called a forming process and its transition voltage is called the forming voltage.

Unlike other transition-metal-oxide films, sample A does not require a forming process for resistive switch-

ing. The V_{SET} of sample A measured from a single $100 \times 100 \mu\text{m}^2$ electrode ranges from 13.4 V to 13.8 V (Figure 3(a)) while V_{SET} of sample B measured from an electrode with the same size ranges from 11.4 V to 18.6 V (Figure 3(b)), showing a more than ten times larger variation than that of sample A. For sample B, a few measurements show transitions over 15 V, which resemble forming transitions. However, with such a high SET voltage, repetitive switching processes could not be observed. Our Eu_xO_y films show somewhat higher SET switching voltages than those of transition-metal oxides, such as NiO. These differences in SET switching voltage may result from the larger size of the Eu^{2+} or the Eu^{3+} ion in the lattice or from the different electronic properties of f electrons and d electrons, which determine the conduction behaviors in Eu_xO_y and NiO, respectively. Further investigations are necessary.

The V_{RESET} of sample A measured from the same electrode ranges from 2.0 V to 2.5 V and has a distribution comparable to that of V_{SET} of sample A. The V_{RESET} of sample B ranges from 1.8 V to 3.1 V, slightly larger than that of the sample A. Note that the distributions of the V_{SET} and V_{RESET} for both samples do not significantly depend upon the electrode size.

The difference in the distributions of V_{SET} and V_{RESET} between samples A and B may result from the oxygen concentration during the growth because no additional treatments were performed. Like other transition-metal oxides, control of the oxygen partial pressure is necessary to increase repetitive switching. However, surprisingly, the ratios of resistance values of the high-resistance state to those of the low-resistance state for both samples have similar values of 10^8 . Typically, nickel-oxide-based layered structures show at most ratios of 10^5 or 10^6 [2]. From the device point of view, the larger the resistance ratio of the material, the easier the on and off states of each cell of a non-volatile memory array can be discriminated.

Even though the microscopic origin of the resistive switching is still under debate [11–14], a simple phenomenological model based on a random circuit breaker (RCB) can simulate all experimental results presented here [15]. According to Ref. 15 and other literature, both experimental data and simulated data show a V_{SET} distribution that is typically larger than the V_{RESET} distribution, as seen in other transition-metal oxides. However, we observe the V_{SET} distribution to be smaller than or comparable to that of V_{RESET} in our Eu_xO_y samples. These results can also be simulated by adjusting the parameters of the RCB model [16].

III. CONCLUSION

We deposited polycrystalline Eu_xO_y films consisting of Eu_2O_3 and Eu_3O_4 phases on platinized silicon substrates by using an RF magnetron sputtering method.

The Eu_xO_y films showed repetitive unipolar resistive switching behaviors induced by an external voltage. We found that the oxygen partial pressure during the deposition process affected the chemical compositions and resistive switching characteristics of the Eu_xO_y films. The Eu_xO_y films were shown to be possible good candidates for memory elements of RRAM devices due to their high resistance ratio and small distribution of switching voltages.

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