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Influence of oxygen ion drift on a negative difference behavior in a reset process of bipolar resistive switching

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ABSTRACT

We present the oxygen ion drift-based resistive switching features of TiO_x/TiO_y bi-layer homo-junctions. The TiO_x layer in this bi-layer configuration was designed to have a stoichiometric chemical composition of TiO_2, while the TiO_y layer was designed to have a non-stoichiometric chemical composition. X-ray photoelectron spectroscopy measurements were carried out before and after electro-forming to determine the role of non-lattice oxygen content. Variation of the oxygen ion content in the TiO_2 layers resulted in changes in the on/off ratio and increased the non-lattice oxygen content. A possible switching mechanism based on oxygen ion content is discussed.

1. Introduction

Resistive switching behaviors observed in various oxide materials have attracted considerable attention because of the simple metal/oxide/metal sandwich structures of these materials and their potential applications in next-generation nonvolatile memory devices (NVMs) [1–4]. Resistive switching can be generally classified into two types based on the polarity of the applied voltage. One type is bipolar resistive switching (BPS), in which the set and reset voltages have opposite polarities, while the other is unipolar resistive switching (UPS), in which the set and reset voltages have the same polarity [5]. Although these two switching types have their respective advantages and disadvantages, BPS behaviors have been studied intensively, because the BPS behaviors have a low reset current and excellent endurance characteristics, which are essential characteristics of resistive switching random access memory (ReRAM) devices [4,6,7]. A variety of semiconductor oxides such as ZrO_x, TiO_x, TaO_x, HfO_x, and AlO_x have also been reported to show BPS [8–12]. Although the actual switching mechanism of BPS is not yet well understood, it is commonly believed that the origin of reversible resistive switching depending on bias polarity in BPS can be attributed to the migration of oxygen vacancies (ions). In our previous study, we showed that in $Pt/TiO_x/TiO_y/Pt$ homo-junctions, the origin of BPS was the formation and annihilation of Ti-based sub-oxide phases with a changing Ti electronic binding state induced by the drift of positively charged oxygen vacancies (or negatively charged oxygen ions) at the TiO_x/TiO_y interface region [13].

We therefore investigated the switching behavior of bi-layer TiO_x/TiO_y homo-junctions with different oxygen ion contents in the TiO_x layer while fixing the oxygen content in the TiO_y layer. Based on our findings, we propose a role for non-lattice oxygen ions in the reset process. Non-lattice oxygen ions were observed by X-ray photoelectron spectroscopy (XPS).

2. Experiments

$Pt/TiO_x/TiO_y/Pt$ metal–oxide–metal matrix samples with different oxygen contents in the Ti oxide layers (TiO_x as an oxygen rich layer, TiO_y as an oxygen poor layer) were prepared as test resistance switching cells. First, Pt bottom electrodes with a thickness of 100 nm were deposited by a DC sputtering system on SiO_2/Si commercial substrates at room temperature. Before the

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deposition of Pt bottom electrodes, 50-nm thick Ti buffer layers were prepared on top of the SiO_2/Si substrates using the same system. Then, 15-nm thick TiO_y oxygen poor layers were grown on the Pt bottom electrode using a RF sputtering technique in a pure Ar atmosphere with a TiO_2 ceramic target. Various TiO_x layers of the same thickness were deposited under different oxygen gas rates in the oxygen and Ar mixture atmosphere as oxygen-rich layers. The ratio of the oxygen gas partial pressure to the working pressure was varied from 10% to 70% to obtain TiO_x films with different oxygen contents. Finally, a Pt top electrode with a thickness of 100 nm was prepared by a lift-off photolithographic process to form device patterns of 50 μm × 50 μm dots. Electrical measurements were taken using a Keithley 4200 semiconductor parameter analyzer at room temperature. Stoichiometric amounts of Ti and O atoms in the TiO_x and TiO_y layers were confirmed by Rutherford backscattering spectrometry (RBS) measurements. High-resolution transmission electron microscopy (HRTEM) images for structural analysis are also presented. As mentioned above, XPS measurements to observe non-lattice oxygen ion migration were carried out in the initial state (IS) and low resistance state (LRS) immediately after the forming process. To increase the XPS signal intensity from the formation of conducting filaments in the metal oxide, two different resistance states (IS, LRS), each with an area of 200 × 200 μm^2, were created separately by applying a switching voltage and scanning 400 equally-spaced point-contacts directly on the top TiO_x layer within the area using an Au-coated tungsten probe tip with a diameter of 5 μm.

3. Results and discussion

A typical resistive switching device structure is illustrated in Fig. 1(a). To further clarify the role of migration of oxygen ions in the switching mechanism, the top TiO_x layers were fabricated with different chemical oxygen contents while the chemical oxygen content of the bottom TiO_y layer was fixed at $Ti_1O_{1.39}$. The chemical compositions of the top TiO_x layer in samples A, B, and C are $Ti_1O_{1.5}$, $Ti_1O_{1.85}$, and $Ti_1O_{1.9}$, respectively. Fig. 1(b) shows typical current–voltage (I–V) curves of BPS for samples A, B, and C. All samples required an electric forming process for clear BPS and after the forming process, the resistance state of the samples switched to a LRS (data not shown). After the forming process, when a sweep voltage from zero to negative was applied to the top electrode, a sudden increase in resistance (defined as the reset process) from the LRS to the high resistance state (HRS) took place at about −1.1 V. As the applied voltage swept from negative to zero, the HRS was maintained in all samples. When the applied voltage swept from zero to positive, a decrease in the resistance from the HRS to the LRS (defined as the set process) was observed at about 0.8 V. As the applied voltage swept from positive to zero, the LRS was maintained. During this resistive switching process, all samples showed similar resistive switching I–V characteristics, including similar set and reset voltages and the same switching direction. However, the resistance values of the HRS increased from samples A to C while the resistance values of the LRS remained at a similar level. Thus the on/off ratios of the LRS and HRS also increased from samples A to C.

To examine the relationship between oxygen chemical composition and the on/off ratio in BPS, high resolution XPS analysis of the top TiO_x layer in samples A, B, and C was investigated in the IS (before forming) and LRS (after forming) (Fig. 2). Non-lattice oxygen (NLO) in the core level spectra of O 1s indicates the existence of oxygen vacancies (V_O), while lattice oxygen (LO) indicates the Ti–O binding state [14,15]. Fig. 2(a) shows the XPS core-level spectra of O 1s for the IS for samples A, B, and C. Peak deconvolution analysis revealed that the electron binding energies for LO and NLO in the top TiO_x layer were 529.7 eV and 531.6 eV, respectively. As shown in Fig. 2(a), all samples had a similar composition ratio of LO and NLO. However, in Fig. 2(b), after the forming process, the NLO signal increased with increasing oxygen contents in the TiO_x layer. This increase in NLO content from samples A to C is proportional to the increase in movable oxygen vacancies or ions in the top TiO_x layer when an external electronic bias was applied to the samples.

To gain a better understanding of the role of oxygen vacancies (or ions) in resistive switching behavior, we analyzed the electrical conduction mechanism, before and after the reset process, by fitting current–voltage (I–V) curves of the reset process in Fig. 1(b) with different conduction mechanisms. As depicted in Fig. 3(a) plotted on a double-logarithmic scale, the I–V curves for the LRS and low voltage region in the HRS are well described by ohmic conduction behavior, where the shops are approximately 1. This ohmic conduction is a result of connected conduction filaments between the top and bottom electrodes in the LRS and their residuals in the HRS [16,17]. However, the electrical conduction for the HRS in the high voltage region is best described by a trap-controlled space-charge-limited-conduction (TC-SCLC) mechanism [18–20]. As shown in Fig. 3(b), a power law behavior of I–V characteristics ($I \propto V^n$) was observed with a slope (n) that increased from 1.8 in sample A to 2.9 in sample C. The value of the slope is an indication of the concentration of traps in the energy band gap [21–23]. Thus, a greater oxygen chemical content in the TiO_x layer leads to more movable oxygen vacancies (or ions) and trap states in the oxide layer during the forming process, and these oxygen vacancies (or ions) and trap states enhance the reset process by increasing the on/off ratio of the LRS and HRS.

High magnification cross-sectional TEM images of the IS and HRS of sample C, which had the largest on/off ratio, are displayed in Fig. 4(a) and (b), respectively. As shown in Fig. 4(a), the entire

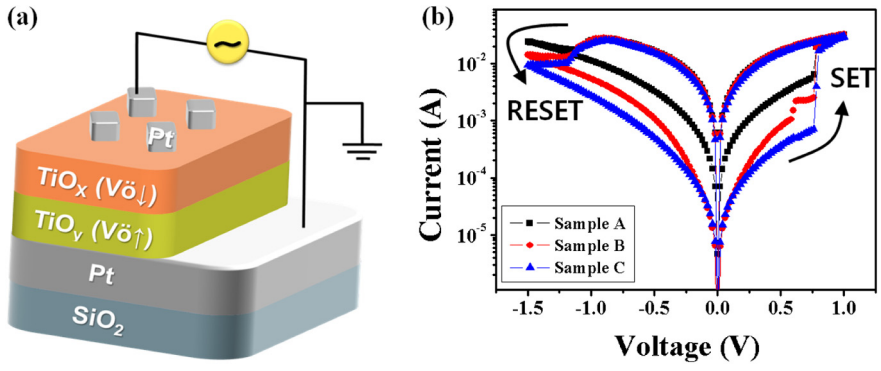

Fig. 1. (a) Schematic layout of a Pt/TiO_x/TiO_y/Pt bi-layer structure cell. (b) Resistance switching characteristics of various samples with different oxygen contents.