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Bipolar resistive switching of chromium oxide for resistive random access memory

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ABSTRACT

This study investigates the resistance switching characteristics of Cr_2O_3-based resistance random access memory (RRAM) with Pt/Cr_2O_3/TiN and Pt/Cr_2O_3/Pt structures. Only devices with Pt/Cr_2O_3/TiN structure exhibit bipolar switching behavior after the forming process because TiN was able to work as an effective oxygen reservoir but Pt was not. Oxygen migration between Cr_2O_3 and TiN was observed clearly before and after resistance switching from Auger electron spectroscopy (AES) analysis. Both low resistance state, ON state, and high resistance state, OFF state, of Pt/Cr_2O_3/TiN structures are stable and reproducible during a successive resistive switching. The resistance ratio of ON and OFF state is over 10^2, on top of that, the retention properties of both states are very stable after 10^4 s with a voltage of -0.2 V.

1. Introduction

Conventional nonvolatile floating memories are expected to reach certain technical and physical limit in the future, therefore the next generation nonvolatile memory has been studied aggressively [1]. Furthermore, new concepts for high density and high-speed nonvolatile memory devices have been studied extensively, including a nanofloating gate memory (NFGM) [2], a polymer random access memory (PoRAM) [3], a magneto-resistive RAM (MRAM) [4] and a resistive RAM (RRAM) [5–10]. Among these memories, RRAM was considered to be the most promising candidate, owing to advantages of its simple structure, low operating power, fast switching speed and high density. Various materials have been demonstrated to possess resistive switching characteristics, such as Cu_2S [5], Al_2O_3 [6], NiO [7], HfO [8], PCMO [9], and $RbAg_4I_5$ [10].

In most studies, oxygen interaction between metal oxide and metal electrode has been reported as the dominant mechanism for switching behavior [6–8,11]. Due to the standard potential of different material's effective influence on reaction and reduction, it is considered that the operation voltage will be dependent on the standard potential [12]. Thus, the standard potential plays important roles in the resistance switching property. In many literatures, Al_2O_3 and NiO have been proposed to show resistance switching behavior [6,7,13,14]. The goal is to find a resistance switching layer with lower operation voltage and acquire the reliability that'll be able to sustain the same on/off ratio after long period of operation. In this study, the Cr_2O_3 dielectric was proposed as a reversible resistance switching layer because the standard potential of Cr/Cr^{3+} couple is -0.74 V vs. normal hydrogen electrode (NHE) is between Al/Al^{3+} couple is -1.66 V vs. NHE and Ni/Ni^{2+} couple is -0.25 vs. NHE. Memory devices with Pt/Cr_2O_3/TiN and Pt/Cr_2O_3/Pt structures were studied to discuss resistance switching mechanism because TiN reacts with oxygen easily but Pt does not [15]. In addition, Auger electron spectroscopy (AES) analysis was used to observe oxygen migration between Cr_2O_3 and TiN before and after resistance switching. It is helpful to understand the resistance switching mechanism. The result demonstrated stable and reproducible resistive switching phenomenon in Pt/Cr_2O_3/TiN structure under atmospheric conditions with a resistance ratio above 10^2, illustrating that Cr_2O_3 thin films have a promising potential for NVM applications.

2. Experiment

The proposed resistive switching memory devices were fabricated on Pt/Ti/SiO2/Si and TiN/SiO2/Si substrates. The resistance switching layer, a 15-nm-thick Cr_2O_3 thin film, was

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deposited by sputtering a chromium target (99.9% pure) with a RF power of 100 W in argon and oxygen mixed gas ambient (Ar/O_2 = 30 sccm/30 sccm) at room temperature. After the Cr_2O_3 deposition, a 140-nm-thick Pt top electrode was deposited through a metal shadow mask by sputtering. The current–voltage (*I–V*) characteristics of memory devices were measured by Keithley 4200 semiconductor characterization system at room temperature. During the electrical measurement, a bias voltage was applied to the top electrode, while the bottom electrode was grounded.

3. Discuss and result

The composition of the as-deposited chromium oxide thin film on $TiN/SiO_2/Si$ subtract without Pt top electrode was analyzed by X-ray photoelectron spectroscopy (XPS). It was performed by using a monochromatic Al Kα (1486.6 eV) X-ray and calibrated by C 1 s peak at 284.5 eV. From the XPS analysis, the binding energies for Cr $2p_{3/2}$ and $2p_{1/2}$ were obtained at 576.4 eV and 586.8 eV, respectively. It was estimated to be Cr_2O_3 [16,17]. Fig. 1a and b show the current–voltage (*I–V*) curves of a device with $Pt/Cr_2O_3/TiN$ and $Pt/Cr_2O_3/Pt$ structure under the cycling DC voltage sweeping operations. Before cycling operations, the irreversible forming processes, as shown in the inserts, were performed by applying a negative DC voltage to the top Pt electrode with a current compliance of 1 mA. Due to the formation of conduction path(s) the apparent increase of current occurred at the voltage of −10 V in $Pt/Cr_2O_3/TiN$ and −8 V in $Pt/Cr_2O_3/Pt$ device can be seen. During the forming process, the initial resistance state is transformed from an initial high resistance state, IHRS, to a low resistance state, LRS. After the forming process, the repeated hysteretic resistance switching behavior was observed only in the $Pt/Cr_2O_3/TiN$ device, shown in four steps in the figure. When the applied voltage raises from 0 to 1.3 V during the reset process, most resistance states start to transform from LRS to high resistance state, HRS, at a reset voltage of 0.6 V. Conversely, as the applied voltage sweeps from 0 to −1.5 V in the set process, an abrupt increase in current is observed at about 0.7 V. Most resistance states start to transform from HRS to LRS and achieved the nonvolatile resistance switching. In the set process, compliance current of 1 mA is applied to prevent a device breakdown. The resistance ratio of two resistance states, HRS/LRS, is about 100 times at a reading voltage of −0.2 V. However, $Pt/Cr_2O_3/Pt$ devices do not exhibit bipolar resistive switching behaviors as shown in Fig. 1b. After the forming process, the resistance state transforms from IHRS to LRS. But the resistance state does not transform from LRS to HRS even with another reset process. It should be noted that $Pt/Cr_2O_3/TiN$ devices exhibit bipolar resistive switching behaviors but $Pt/Cr_2O_3/Pt$ devices do not. TiN can be an effective oxygen reservoir since it can react with oxygen readily. On the contrary, Pt is an inert metal which does not easily react with oxygen [15].

Fig. 2a and b show the Auger electron spectroscopy analysis of $Pt/Cr_2O_3/TiN$ devices with LRS and HRS. Comparing to HRS, the oxygen intensity increases in TiN and decreases in Cr_2O_3 in LRS. It is considered that a negative voltage is applied to the top electrode in the set process. The electrical field ruptures Cr–O bonds and induces the oxygen ions moved from Cr_2O_3 to reserve in TiN. It is due to the fact that the Cr_2O_3 film is nonstoichiometric and there are a large amount of oxygen vacancies in the Cr_2O_3 film. On the contrary, in the reset process, oxygen ions are extracted from TiN and moved from TiN to Cr_2O_3. The oxygen intensity decreases in TiN and increases in Cr_2O_3 in HRS for that reason.

Based on the above observations, a physical model is proposed to illustrate the resistive switching behaviors with a different operating voltage. During the forming process, a negative voltage is applied onto the top electrode, and soft-breakdown occurs while Cr–O bonds rupture at a critical voltage. Thereby, an oxygen vacancy filament is formed in the insulating oxide film to act as a conduction channel, as shown in Fig. 3a. Carriers can travel through vacancies by hopping and the devices would then switch to LRS. Contrarily, when applying a positive bias, oxygen ions are extracted from TiN bottom electrode and recovered with the oxygen vacancies (i.e., Cr–O bonds form again) near the TiN interface, as shown in Fig. 3b. The conducting oxygen vacancy filament ruptures at the interface between TiN and Cr_2O_3 and devices switched to HRS in the reset process. As a result, by applying a different polarity bias on devices, the bipolar resistive switching behavior can easily be obtained due to the generation and recovery of oxygen vacancies at the interface of TiN electrode and Cr_2O_3 dielectric. In previous literature, similar using oxygen vacancies generation and recombination to format/rupture a conduction filament to switch the resistance states is reported in some oxide-based RRAM [18,19].

The retention and endurance were tested to further investigate the reliability characteristics of the memory device. The endurance properties of the memory device is shown in Fig. 4a in which short pulse applied are −1.6 V amplitude 4 μs wide and 1.7 V amplitude 5 μs to switch the devices to on state and off state, respectively. The resistances were extracted at a reading voltage of −0.2 V at room temperature. The result indicates that there is no apparent degradation on resistance ratio after 6×10^4 operation cycles. In addition, after 100 DC sweep cycling the retention properties of LRS and HRS at 85 °C were measured as shown in Fig. 4b. The resistance values of HRS and LRS were very stable even after 10^4 s. The device with $Pt/Cr_2O_3/TiN$ structure owns a good reliability for memory application.

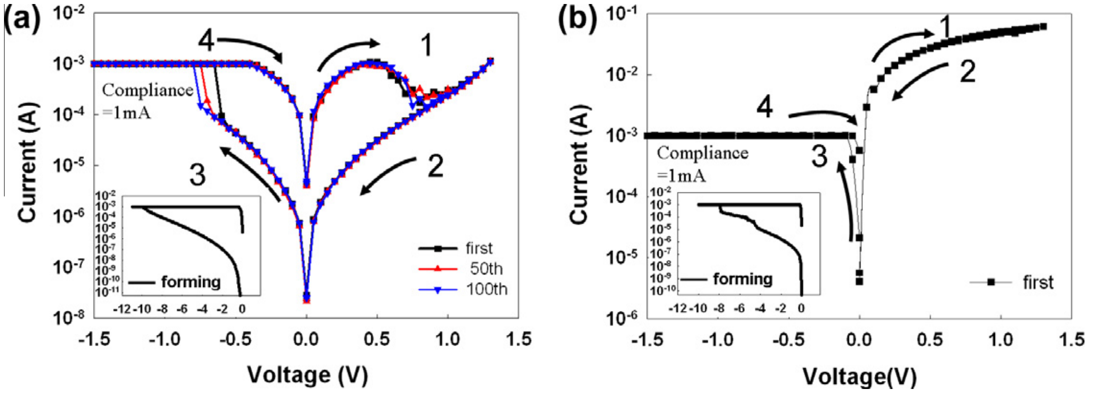

Fig. 1. Typical bipolar *I–V* characteristics at room temperature of (a) $Pt/Cr_2O_3/TiN$ memory device and (b) $Pt/Cr_2O_3/Pt$ memory device.

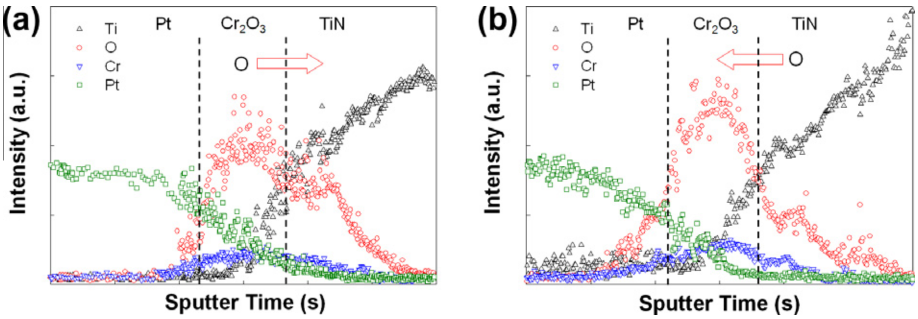

Fig. 2. Auger electron spectroscopy (AES) analysis of Pt/Cr_2O_3/TiN devices with (a) low resistance state (LRS) and (b) high resistance state (HRS).

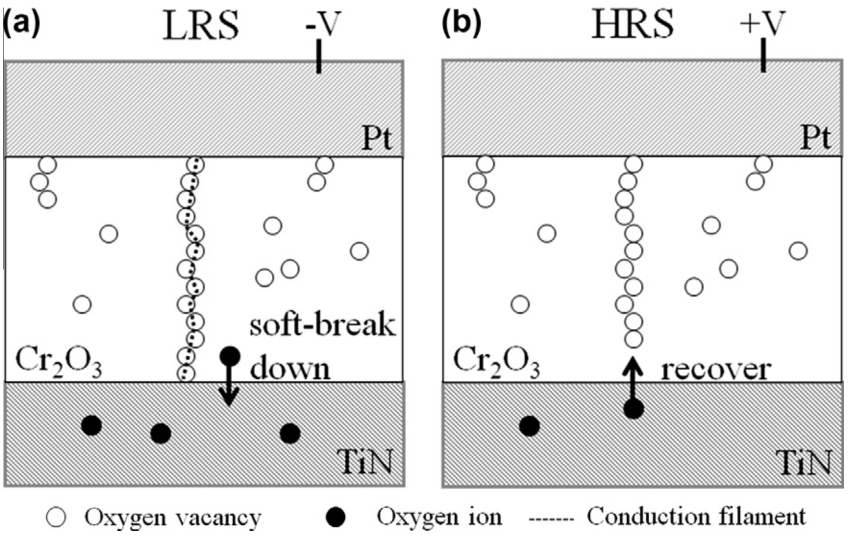

Fig. 3. Distribution of oxygen vacancies in the device: (a) low resistance state (LRS) and (b) high resistance state (HRS).

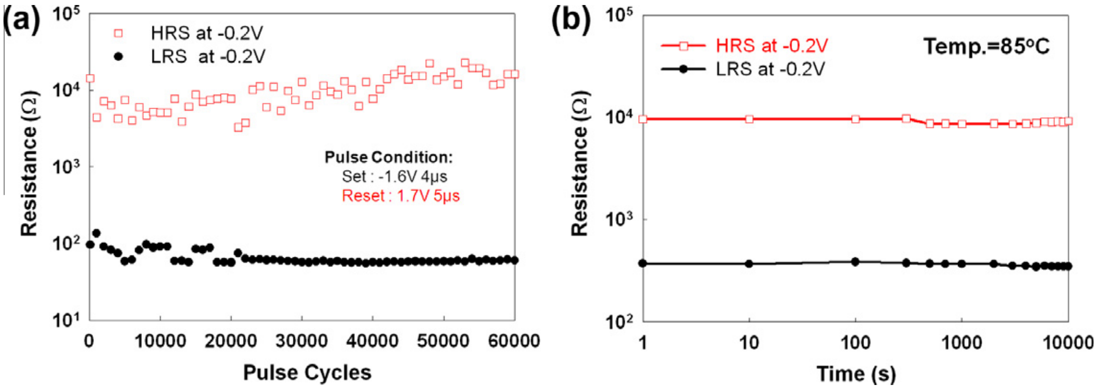

Fig. 4. (a) Endurance performance of the Cr_2O_3 memory device at room temperature and (b) retention characteristics of the device at 85 °C. Reading voltage was −0.2 V.

4. Conclusions

The Pt/Cr_2O_3/TiN and Pt/Cr_2O_3/Pt structures were fabricated for the nonvolatile resistance switching memory application by sputtering a chromium target in an Ar/O_2 environment at room temperature. Before the resistance switching, a forming process is necessary. Only the device with TiN electrode exhibits bipolar resistive switching behaviors because TiN is an effective oxygen reservoir. Observing oxygen migration from Auger electron spectroscopy analysis, a physical model about oxygen vacancy filaments formation and rupture is proposed to illustrate the resistive switching behaviors. The ratio of resistance of ON and OFF state is over 10^2. The endurance and retention results indicate that the proposed memory device has excellent device reliability. Therefore, Cr_2O_3 has a high potential for application in resistance random access memory in the future.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.sse.2010.12.014.

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