Bipolar resistive switching of chromium oxide for resistive random access memory

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Article info

Article history:
Received 15 September 2010
Received in revised form 8 December 2010
Accepted 22 December 2010
Available online 4 February 2011

The review of this paper was arranged by Prof. A. Zaslavsky

Keywords:
Cr2O3 thin film
Resistance switching
Nonvolatile memory

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 CuS [5], Al2O3 [6], NiO [7], HfO [8], PCMO [9], and RbAg3I5 [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, Al2O3 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 Cr2O3 dielectric was proposed as a reversible resistance switching layer because the standard potential of Cr/Cr3+ couple is –0.74 V vs. normal hydrogen electrode (NHE) is between Al/Al3+ couple is –1.66 V vs. NHE and Ni/Ni2+ couple is –0.25 V vs. NHE. Memory devices with Pt/Cr2O3/TiN and Pt/Cr2O3/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 Cr2O3 and TiN before and after resistance switching. It is helpful to understand the resistance switching mechanism because TiN reacts with oxygen easily but Pt does not [15].

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 Cr2O3 thin film, was
behaviors as shown in Fig. 1b. After the forming process, the resistance of TiN/SiO2/Si subtract without Pt top electrode was analyzed by a 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/SiO2/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 1s peak at 284.5 eV. From the XPS analysis, the binding energies for Cr 2p3/2 and 2p1/2 were obtained at 576.4 eV and 586.8 eV, respectively. It was estimated to be Cr2O3 [16,17]. Fig. 1a and b show the current–voltage (I–V) curves of a device with Pt/Cr2O3/TiN and Pt/Cr2O3/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/Cr2O3/TiN and −8 V in Pt/Cr2O3/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/Cr2O3/TiN device, as 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. The resistance ratio of two resistance states, LRS and HRS at 85 °C were measured as shown in Fig. 4b. The resistances were extracted at a reading voltage of 0.2 V at 104 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 104 s. The device with Pt/Cr2O3/TiN structure owns a good reliability for memory application.

Fig. 1. Typical bipolar I–V characteristics at room temperature of (a) Pt/Cr2O3/TiN memory device and (b) Pt/Cr2O3/Pt memory device.
4. Conclusions

The Pt/Cr$_2$O$_3$/TiN and Pt/Cr$_2$O$_3$/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$_2$O$_3$ has a high potential for application in resistance random access memory in the future.

Acknowledgements

This work was performed at National Science Council Core Facilities Laboratory for Nano-Science and Nano-Technology in Kaohsiung-Pingtung area and supported by the National Science Council.
Appendix A. Supplementary material


References