Gradually Modified Conductance in Self-Compliance Region of Atomic-Layer-Deposited Pt/TiO₂/HfAlO_x/TiN RRAM Device

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Nano Express

Keywords: Resistive switching, synaptic device, self-compliance, bilayer stack

Posted Date: July 2nd, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-660171/v1>

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Abstract

This study presents conductance modulation in a Pt/TiO₂/HfAlO_x/TiN resistive memory device in the compliance region for neuromorphic system applications. First, the chemical and material characteristics of the atomic-layer-deposited films were verified by X-ray photoelectron spectroscopy depth profiling. The low-resistance state was effectively controlled by the compliance current, and the high-resistance state was adjusted by the reset stop voltage. Stable endurance and retention in bipolar resistive switching were achieved. When a compliance current of 1 mA was imposed, only gradual switching was observed in the reset process. Self-compliance was used after an abrupt set transition to achieve a gradual set process. Finally, 10 cycles of long-term potentiation and depression were obtained in the compliance current region for neuromorphic system applications.

Introduction

Resistive-switching behavior is observed in many dielectrics under an electric field [1]. The non-volatile resistance states are reversible in the high-resistance and low-resistance states. The types of switching are largely divided into unipolar and bipolar switching [2]. The memory state of the unipolar resistive-switching memory can be changed by the electric stress at the same polarity. The reset process from a low-resistance state (LRS) to a high-resistance state (HRS) occurs by the rupture of the conducting filament by Joule heating [3]. In contrast, the set and reset processes of the bipolar resistive type occur via the opposite polarity of the electric field. Among the many resistive-switching materials, metal oxides are the most popular owing to their good stability, reproducibility, and repeatability [4–13]. Representative metal oxide-based resistive random-access memory (RRAM) materials include TaO_x, TiO₂, Al₂O₃, and HfO₂ [4–13]. It is worth noting that a bilayer stack of metal oxide exhibits relatively better resistive-switching performances, such as endurance, retention, and variability performances, compared with a single-layer stack [14–18]. In a previous study, low-power operation was achieved by controlling oxygen vacancies in the case of HfO₂/TiO_x bilayer RRAM [16]. In another study, the switching uniformity was improved for a HfO₂/TiO₂ bilayer device owing to stabilized filament formation and rupture [Semicond. Sci. Technol. 31 (2016) 105005]. In the case of a double insulating layer sandwiched by electrodes with a large difference in work function, self-rectifying I-V curves have been reported, which can reduce the sneak current in the cross-point array [18].

Resistive-switching dielectrics can be deposited by various methods, such as sputtering. Atomic layer deposition (ALD) systems have the advantages of uniform deposition, excellent step coverage, and accurate thickness control [19]. Therefore, it is suitable for a 3D vertical RRAM structure [20] as well as a conventional 2D cross-point RRAM structure.

Neuromorphic systems are being studied to implement a better and more efficient computing system than the existing von Neumann computing structure [21]. Neuromorphic computing enables data operation and storage to be processed as closely as possible. Parallel data processing with low energy is achieved by adopting a structure in which the RRAM element array acts as an artificial synapse [22–26].

To implement a RRAM-based synaptic array in a neuromorphic system, it is important that the state of RRAM has a multi-level cell (MLC). It is important to gradually change the conductance value of a RRAM device while repeatedly imparting pulses of the same voltage and width. To achieve a gradual change, the current of a RRAM cell should not be changed abruptly by the applied electric field. Filamentary-type resistive switching generally exhibits an abrupt transition in the set process [27]. There have been reports of a gradual transition in the set process using a bilayer stack [28, 29]. A Ti/TaO_x/HfO₂/Pt device exhibits gradual set and reset processes owing to the oxygen reservoir of the thin TaO_x layer [28]. In addition, a Ni/SiN/Al₂O₃/TiN device shows gradual set and reset I-V characteristics due to the tunnel barrier of Al₂O₃ [29]

In this study, we demonstrate the gradual synaptic modulation in an ALD-deposited TiO₂/HfAlO_x RRAM device. First, the ALD-deposited layers and TiN bottom electrode were verified by X-ray photoelectron spectroscopy (XPS) depth analysis. Stable resistive switching was achieved in a typical bipolar resistive-switching operation. The HRS and LRS were gradually controlled by increasing the reset stop voltage. Self-compliance was observed, and a gradual set was achieved when the operation current was increased to approximately 2 mA during the set process. Finally, by the set pulses and reset pulses, ten conductance increase and decrease changes were achieved.

Methods

A Pt/TiO₂/HfAlO_x/TiN RRAM device was prepared as follows. A hundred-nanometer-thick TiN layer was deposited on a SiO₂/Si wafer via reactive sputtering. Moreover, a seven-nanometer-thick HfAlO_x layer was deposited by the ALD system. Tetrakis (ethylmethylamino) hafnium (TEMAH) and trimethylaluminum (TMA) were used as the metal precursors for the HfO₂ and Al₂O₃ layers, respectively. H₂O was used as the oxidant for both layers. Eleven cycles of (TMA + H₂O) deposition and one cycle of (TEMAH + H₂O) deposition were conducted for the alloyed-type dielectric. Next, a seven-nanometer-thick TiO₂ layer was deposited using titanium tetraisopropoxide (TTIP) and H₂O as reactants. Finally, a hundred-nanometer-thick Pt layer was deposited using an electron-beam evaporator via a shadow mask possessing circular patterns of 100 μm diameter. XPS depth analysis was conducted using a Nexsa photoelectron spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) with a microfocus monochromatic X-ray source (Al-Kα (1486.6 eV)), a sputter source (Ar⁺), an ion energy of 2 kV, a sputter rate of 0.5 nm/s for SiO₂, and a beam size of 100 μm.

Results And Discussion

Figure 1a shows a schematic of the Pt/TiO₂/HfAlO_x/TiN device. XPS analysis was performed as the X-ray was incident from the TiO₂ surface, and analysis was conducted on the inner thin film through Ar⁺ etching. Figures 1b and c show the Ti 2p spectra for etch level 2 and etch level 35, which correspond to the TiO₂ layer and TiN bottom electrode, respectively. The Ti 2p XPS spectra include Ti 2p_{3/2} and Ti2p_{1/2},

as shown in Figs. 1b and c. The peak binding energies of Ti 2p_{3/2} and Ti 2p_{1/2} are located at approximately 458.94 eV and 464.5 eV for Ti-O bonds [30]. However, the peak binding energies of Ti 2p_{3/2} and Ti 2p_{1/2} are found at approximately 454.92 eV and 460.93 eV for Ti-N bonds [31]. Figure 1d shows the Hf 4f spectra at an etch level of 9. Hf 4f_{7/2} and Hf 4f_{5/2} doublet peaks are found at 18.63 eV and 20.03 eV, respectively, for Hf-O bonds in the Hf-dominated HfAlO_x film. Figure 1e shows the Al 2p spectra at an etch level of 9. Because the Al content is low in the HfAlO_x film, the Al intensity is low and some noise is observed, but a distinct peak is observed for the Al-O bond at approximately 75.4 eV [12].

Figure 2a shows the I-V current characteristics, including 200 cycles of the Pt/TiO₂/HfAlO_x/TiN device. The set process occurs by sweeping from 0 V to -0.7 V. An abrupt set transition is observed from the HRS to LRS in which the decrease in resistance is due to soft breakdown in the two insulator layers. Here, a compliance current (CC) of 1 mA was used to tightly control the conducting filament. Moreover, the oxygen vacancies in the double insulating layers were created under the applied bias. It should be noted that the negative bias on the Pt/TiO₂/HfAlO_x/TiN device is relatively more favorable for resistive switching because the TiON interfacial layer acts as an oxygen reservoir. The oxygen can easily move to the TiN layer to form TiON when a negative bias is applied on Pt. The detailed mechanisms are discussed in previous studies [32]. The reset process is conducted to return the device to the HRS by sweeping from 0 V to 1 V. The reset process occurs because of the rupture of the conducting filament based on oxygen vacancies. The oxygen ions move from the TiON layer under a positive bias, and the recombination occurs with oxygen vacancies. Subsequently, the conducting filament can be ruptured, which indicates a decrease in conductance. On the other hand, resistive switching is not fluent under the opposite polarity bias (not shown here) because Pt, which is an inert metal, is less reactive toward oxygen than TiN. Figure 2b shows up to 200 cycles in which LRS and HRS possess a read voltage of 0.3 V. Uniform LRS and HRS are achieved even though a small on/off ratio is observed. To increase the on/off ratio, the CC and reset stop voltages can be increased. The LRS current increases with an increase in CC, and the HRS current decreases with an increase in the reset stop voltage. An on/off ratio of 10 times or more was achieved by a CC of 10 mA and reset sweep voltage of 2 V for 200 endurance cycles, as shown in Fig. 2c. Good retention properties in the LRS and HRS were observed for 1 h (Fig. 2d).

Next, we demonstrate the fine modulation of the LRS and HRS by varying the reset stop voltage. Figures 3a–c show the I-V characteristics of the Pt/TiO₂/HfAlO_x/TiN device with reset stop voltages of 1.1 V, 1.2 V, and 1.3 V, respectively. Stable and uniform switching is observed for 21 cycles in each case. It is noted that the LRS and HRS currents decrease with the reset stop voltage. The higher the voltage, the more the conducting filament ruptures, and thus, the HRS current decreases. It is also observed that the current gradually decreases as the reset stop voltage increases in the DC sweep mode, as shown in Fig. 3e. However, MLC can be achieved by CC for the set process, which is not desirable for device control.

To overcome the limitation of the abrupt set process, we used different current regions in self-compliance for the gradual set process. Figure 4a shows the self-compliance curve after the CC controlled I-V curves of the Pt/TiO₂/HfAlO_x/TiN device. The self-compliance region is clearly observed on the linear scale in

Fig. 4b. The current gradually increases with the voltage in the self-compliance region after an abrupt transition from 432.7 μA to 2 mA at -0.55 V. This gradual transition region is suitable for achieving MLC. The self-compliance behavior during set transition due to the TiON layer acts as a series resistance [33]. Furthermore, the gradual reset switching is maintained after the self-compliance set process.

Next, the potentiation and depression characteristics were mimicked to apply the Pt/TiO₂/HfAlO_x/TiN device to a neuromorphic system. For potentiation, repetitive pulses with a voltage of -0.8 V and a width of 1 ms were used, as shown in Fig. 5. A low read pulse voltage (0.3 V) was used to not affect the conductance change during the reading. It should be noted that for gradual conductance modulation in the self-compliance region. We demonstrated 10 cycles of long-term potentiation and long-term depression and found no significant degradation of the MLC.

Conclusions

In this study, multilevel cells were achieved in a Pt/TiO₂/HfAlO_x/TiN RRAM device by gradual resistive switching in the compliance region for neuromorphic system applications. The chemical and material characteristics of the TiO₂/HfAlO_x/TiN stack were confirmed by XPS depth profiling. The LRS was varied by the CC at a compliance current of 1 mA, and the HRS was accurately controlled by the reset stop voltage. Repetitive endurance and stable retention characteristics were observed in different compliance current modes. The self-compliance current region was used to improve the gradual resistive switching during the set process. Finally, stable and repetitive long-term potentiation and depression were obtained owing to the gradual resistive switching in the compliance current region for neuromorphic system applications.

Abbreviations

LRS: low-resistance state; HRS: high-resistance state; RRAM: resistive random-access memory; MLC: multi-level cell; CC: compliance current; ALD: atomic layer deposition; TEMAH: tetrakis (ethylmethylamino) hafnium; TMA: trimethylaluminum; TTIP: titanium tetraisopropoxide.

Declarations

Acknowledgements

This work was supported in part by the National Research Foundation of Korea (NRF), and the grant was funded by the Korean government (MSIP) under Grant 2021R1C1C1004422.

Authors' contributions

HR prepared the samples and electrical measurements and wrote the manuscript. SK designed the experiments. All authors read and approved the final manuscript.

Funding

This work was supported in part by the National Research Foundation of Korea (NRF), and the grant was funded by the Korean government (MSIP) under Grant 2021R1C1C1004422.

Availability of data and materials

All data are fully available.

Competing interests

The authors declare that they have no competing interests.

Authors' information

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Figures

Figure 1

a Schematic of Pt/TiO₂/HfAlO_x/TiN device. XPS spectra of TiO₂/HfAlO_x/TiN stack: b Ti 1p for Ti-O bonds c Ti 1p for Ti-N bonds d Hf 4f and e Al 2p.

Figure 2

a I-V characteristics of Pt/TiO₂/HfAlO_x/TiN RRAM device. b Endurance at a compliance current (CC) of 1 mA. c Endurance at a CC of 10 mA. d Retention characteristics for 3600 s.

Figure 3

I-V characteristics of Pt/TiO₂/HfAlO_x/TiN RRAM device at reset stop voltage of a 1.1 V, b 1.2 V, and c 1.3 V. d Read current distribution as a function of reset stop voltage. e MLC by reset stop voltage.

Figure 4

Self-compliance characteristics of Pt/TiO₂/HfAlO_x/TiN RRAM device. a log-scale. b linear scale.

Figure 5

Potentiation and depression characteristics of Pt/TiO₂/HfAlO_x/TiN RRAM device.