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Structural and electrical characteristics of Zr-doped HfO$_2$ (HZO) thin films deposited by atomic layer deposition for RRAM applications

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Abstract: In this study, Zr-doped HfO$_2$ (HZO) based resistive random-access memory (RRAM) device were fabricated. The Hf:Zr (1:1) ratio in the HZO films were controlled by changing the HfO$_2$ and ZrO$_2$ cycle ratio during the atomic layer deposition (ALD) process. Next, we studied the structural and electrical properties of the Au/HZO/TiN RRAM device structure. The RRAM devices exhibits an excellent resistance ratio of the high resistance state (HRS) to the low resistance state (LRS) of ~10^3 A, and as well as good endurance (300 cycles) and retention (>10^3 s), respectively. Further, the device showed different conduction mechanism in LRS and HRS modes. The lower biased linear region is dominated by ohmic conductivity, whereas the higher biased nonlinear region is dominated by a space charge limited current conduction. This device is suitable for application in future high-density nonvolatile memory RRAM devices.

Keywords: non-volatile memory; RRAM; resistive switching; atomic layer deposition; charge transport mechanism

1. Introduction

Resistive random access memory (RRAM), is emerging as an potential candidate for next-generation data storage system [1]. The key features of RRAM are high-speed operation, simple fabrication, low-power consumption, and good-scalability [2,3]. The RRAM devices consist of a simple capacitor-like structure consisting of an insulating/dielectric layer sandwiched between two metal electrodes [4,5]. They exhibit reversible resistive switch behaviour when applied to unipolar or bipolar voltages [6].

In RRAM devices, resistive switching behaviour can be achieved with variety of transition metal oxides (TMOs), including HfO$_2$, ZrO$_2$ TiO$_2$, NiO, and ZnO [7]. In recent years, TMO materials have attracted considerable attention and have been widely investigated due to their excellent resistive switching abilities and simple fabrication process [8]. Among them, the HfO$_2$ and ZrO$_2$ films are extremely promising candidates because of their high dielectric constant, wide band gap, excellent thermal stability and complementary metal oxide semiconductor (CMOS) technology [9,10]. This makes them a significant advantage for integrating resistive switching devices using CMOS technology. Meanwhile, flexible electronic devices that are light weight and flexibility are drawing a lot of attention in the next generation of wearable devices. The thin films based on HfO$_2$/ZrO$_2$ are hence ideal for flexible RRAM applications.

In order to achieve better resistive switching characteristics for memory devices, a doping process is often required to improve endurance performance and uniformity

[11]. Previously, limited studies have been performed on HZO-based RRAM devices [12,13]. However, while HfO$_2$ and ZrO$_2$-based resistive switches perform well in certain areas, their characteristics are still insufficient to meet the application requirements [14]. So far, the resistive switching capabilities of strongly oriented HZO film RRAMs have not been investigated. It is worthwhile to develop highly orientated HZO thin films and test their performance as resistive switching memories. Herein, a low-temperature ALD technique was developed for Zr-doped HfO$_2$ RRAM structures. However, the Au/HZO/TiN RRAM device exhibited significant suppression of leakage currents, and good endurance (>300 cycles) and retention (>10^4 s). Further, the typical conduction mechanisms in Au/HZO/TiN RRAM device are also discussed.

2. Materials and methods

A 10 nm thick HZO film were then deposited on TIN/SiO$_2$/Si substrate by atomic layer deposition (ALD) at substrate temperature of 280 °C using Hf[N(C$_2$H$_5$)CH$_3$]$_4$ (TEMA–Hf), Zr[N(C$_2$H$_5$) CH$_3$]$_4$ (TEMA-Zr), and ozone as the Hf-precursor, Zr-precursor, and oxygen source, respectively. Because HfO$_2$ and ZrO$_2$ have an almost identical ALD growth rate, the HZO films were deposited with a 1:1 ALD cycle ratio. Further, a 50 nm thick Au top electrodes (TE) layer with an area of 100 × 100 μm^2 were deposited by physical vapor deposition followed by metal shadow mask. The schematic diagram of the Au/HZO/TiN RRAM device shown in **Figure 1a**. The electrical characterizations were measured by using semiconductor parameter analyzer (Agilent B1500A) with a room temperature. The measurements were carried out in a dc voltage sweep mode, with all basis voltages applied to the Au electrode while the TiN was grounded.
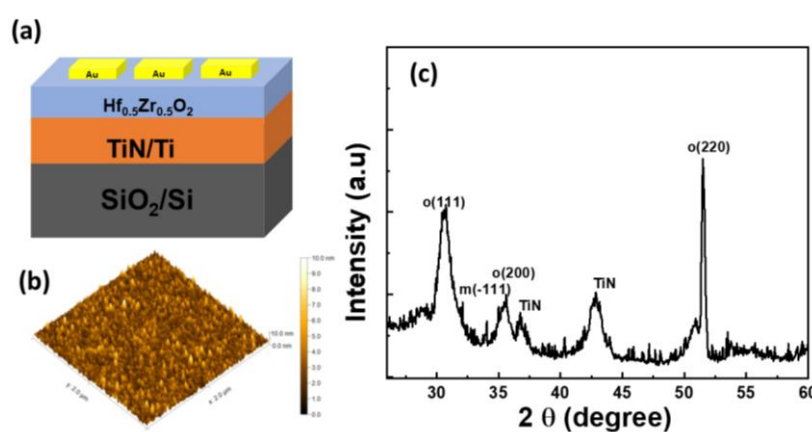

Figure 1. (a) Schematic view of the Au/HZO/TiN RRAM device; **(b)** AFM image of the HZO thin film; **(c)** X-ray diffraction pattern (XRD) analysis.

3. Results and discussions

Figure 1b shows the 3D AFM images of the scan area of 2 μm × 2 μm of HZO thin film. The surface morphology of the HZO thin film root-mean-square (RMS) values of 1.216 nm, which indicate that the thin film surface was uniformly deposited and smoothly. The thicknesses of HZO films control by ALD cycles have a noticeable

effect on the RMS roughness's of the thin films. **Figure 1c** shows the structural characterization of HZO films was investigated using the grazing incidence X-ray diffraction (GI-XRD). The HZO films displayed two crystalline structures: (1) m-phase with reflections of (111), and (–111); (2) o-phase with reflections of (111), (200) and (220). Note that o-phase phase in HZO is mainly responsible for the ferroelectric properties.

Figure 2a,b present the typical current-voltage (*I-V*) characteristics of the Au/HZO/TiN RRAM device structure. The *I-V* characteristics of RRAM device exhibited a clear resistive switching behaviour. The RRAM device displays an excellent resistive switching behaviour with a high on/off ratio of ~10^3. The resistive switching effect was evident since the SET process was detected at TE in the negative voltage directions whereas the RESET process was accomplished at TE with positive polarity. No forming process was necessary for activating the resistive switching effect. For the SET process, the negative voltage was swept in a sequence of 0 V→−3 V and −3 V→0 V. In the first positive bias from 0 V to −3 V, the current of the device increased steadily at −2.34 V for Au/HZO/TiN RRAM, while switching the resistance of device from HRS to LRS. In subsequent negative bias, the resistance change in the devices was retained, indicating non-volatile behaviour. The positive voltage was swept in a sequence of 0 V→3 V and 3 V→0 V for the RESET process. Interestingly, in positive forward bias at 2.72 V for Au/HZO/TiN, the current decreased sharply while the resistance of device switched from LRS to HRS. In subsequent positive bias, the resistance change was maintained throughout the sweep from 3 V to 0 V.
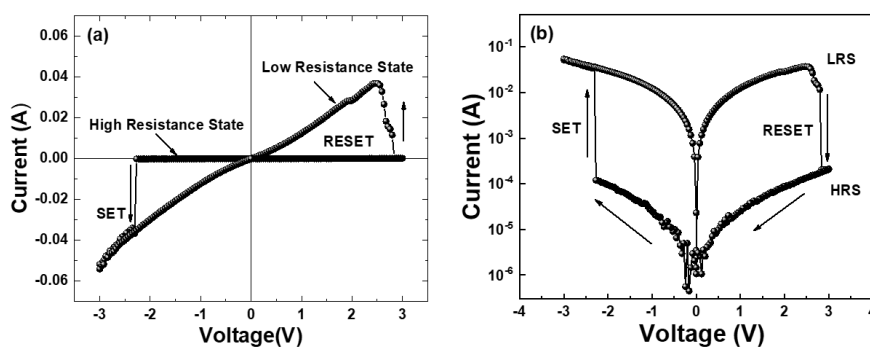

Figure 2. Current-voltage characteristics linear and logarithmic plots of the Au/HZO/TiN RRAM device.

In principle, reliability is an important index to evaluate the function of memory in application. In order to investigate the reliability of the Au/HZO/TiN RRAM devices, the endurance and the retention properties were presented in **Figure 3**. The endurance characteristics of the devices were performed under DC voltage sweeping mode, and the reading voltage was 0.5 V, as presented in **Figure 3a**. The plots clearly illustrate that the RRAM device demonstrate reliable endurance >300 cycles by maintaining a memory window 10^3. Further, the retention stability of the Au/HZO/TiN RRAM device was measured with a readout voltage of 0.1 V, as presented in **Figure 3b**. The retention characteristics of the Au/HZO/TiN RRAM device showed highly stable behaviour up to 10^3 seconds at +0.5 V without any noticeable degradation

Figure 3b. These findings suggest that the Au/HZO/TiN RRAM device has improved endurance and retention characteristics.

To understand the charge transport mechanism in the device, the double logarithmic of current voltage characteristics in both low resistance state and high resistance state is analyzed. **Figure 4a,b** show the positive bias and negative bias region of double logarithmic plots *I-V* characteristics of Au/HZO/TiN RRAM devices. The slope (S) of the curve is labeled by S_1, S_2, and S_3 was observed. In the low voltage region, the *I–V* characteristics exhibits ohmic conduction ($I \propto V$) with a $S_1 \sim 1$ due to the density of thermally generated free carriers is greater than the density of injected charge carriers [15,16]. In the HRS region, the device has a relatively high resistance, and the current flow is relatively small. At lower applied voltages, the current transport is not significantly affected by the resistive switching mechanism, and the conduction can be approximated as ohmic. Further, the values of S_2 increases to >2, such behavior follows from the relation ($I \propto V^2$) and is confirmed by the space charge limited conduction [17]. Finally, the LRS state shows the $S_3 \sim 1$ for Au/HZO/TiN devices, which due to ohmic conduction, indicating the linear behavior of the devices where current is proportional to the voltage is observed [18,19]. However, the Au/HZO/TiN device offers stability and improved migration of oxygen vacancies in the migration in the devices structure.
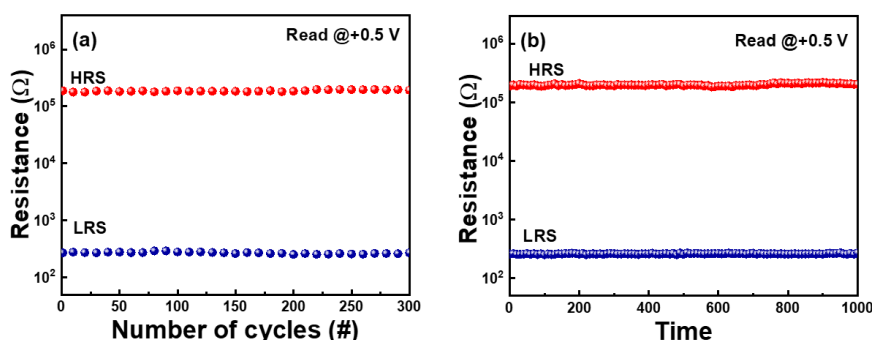

Figure 3. (a) Plot of the resistances of the device at HRS and LRS versus cycle number in the endurance characteristics of Au/HZO/TiN RRAM device; **(b)** Plot of the resistances of the device at HRS and LRS versus time in the retention characteristics time of Au/HZO/TiN RRAM device.
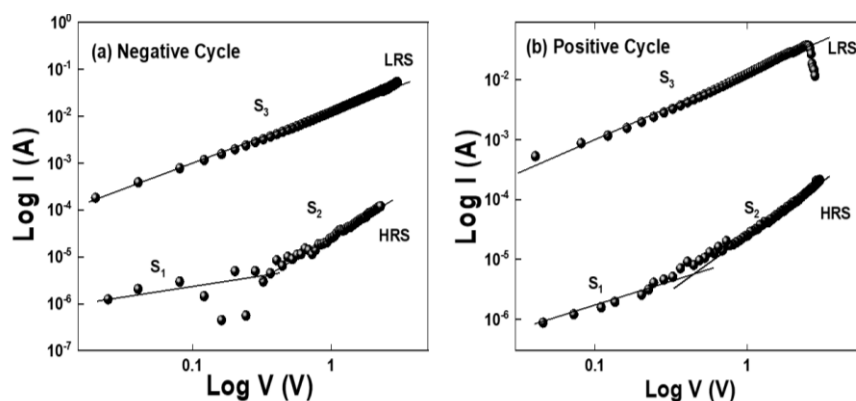

Figure 4. Double logarithmic plot of Au/HZO/TiN RRAM device **(a)** negative cycle and **(b)** positive cycle.

4. Conclusion

In this study, we fabricated and investigated the Au/HZO/TiN based random-access memory (RRAM) device. The RRAM devices showed the excellent stability and good reliability. As prepared device showed an excellent resistive switching behaviour with a high on/off ratio of ~10^3. The endurance test revealed that the devices can be stable for up to 300 cycles, and the retention test revealed that the resistance could be retained at HRS (or LRS) for up to 10^3 s with no fluctuation under a read voltage of 0.1 V. Further, the carrier transport mechanism has been investigated to explain the resistive switching characteristics of Au/HZO/TiN RRAM devices, which shows the LRS and HRS are consistent with the ohmic conduction and space charge limited conduction. This device is appropriate for use in future high-density non-volatile memory RRAM devices.

Conflict of interest: The author declares no conflict of interest.

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