Original Research Article

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 orientated 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,

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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_2H_5)CH_3]$_4$ (TEMA–Hf), Zr[N(C_2H_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.

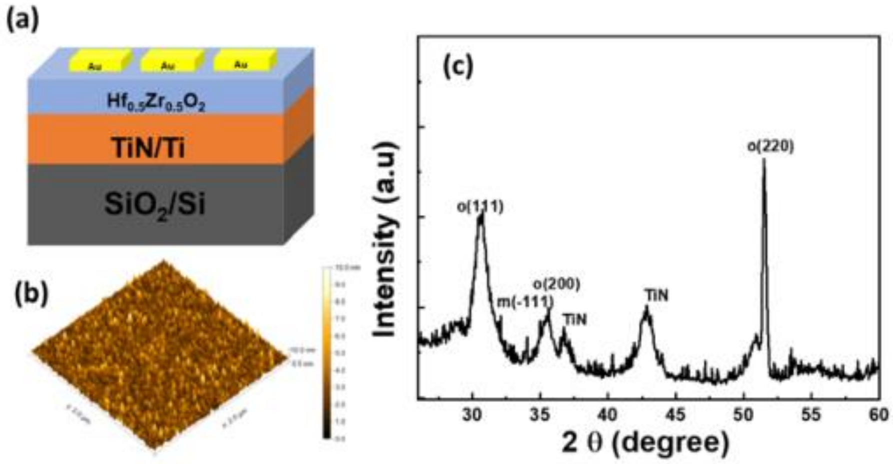

Figure 1 (a) Schematic view of the Au/HZO/TiN RRAM device, (b) AFM image of the HZO thin film, (c) X-ray diffraction pattern (XRD) analysis

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.

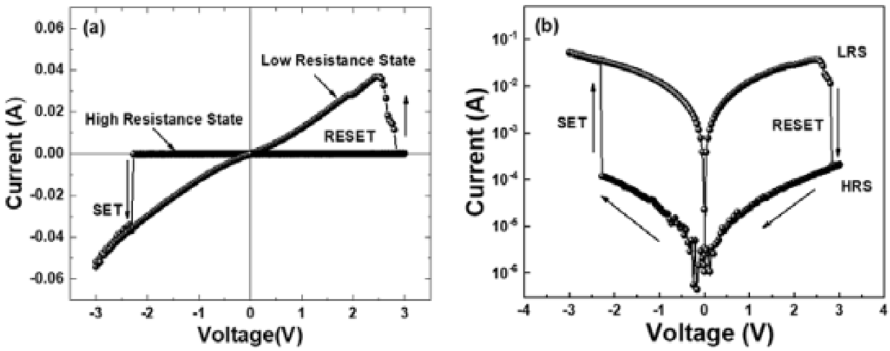

Figure 2 Current-voltage characteristics linear and logarithmic plots of the Au/HZO/TiN RRAM device

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 ~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 ~1 for Au/HZO/TiN devices, which due to ohmic conduction, indicating the linear behavior of the devices where current is proportional tothe 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.

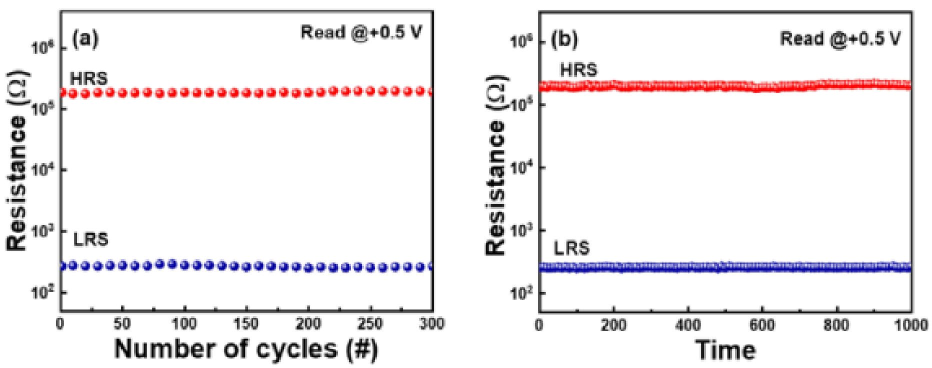

Figure 3 (a) Plot of the resistances of the device at HRS and LRS versus cycle number in the endurance characteristics of Au/HZO/TiN RRAM device.(b) Plot of the resistances of the device at HRS and LRS versus time in the retention characteristics time of Au/HZO/TiN RRAM device

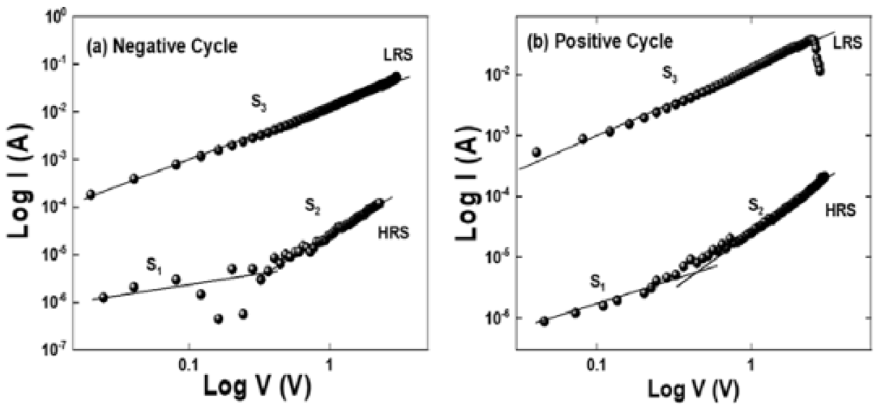

Figure 4 Double logarithmic plot of Au/HZO/TiN RRAM device (a) negative cycle and (b) positive cycle

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 authors declare no conflict of interest.

References

1. Mahata C, Kang M, Kim S. Multi-level analog resistive switching characteristics in tri-layer HfO2/Al2O3/HfO2 based memristor on ITO electrode. Nanomaterials 2020; 10(10): 2069. doi: 10.3390/nano10102069
2. Li Y, Long S, Zhang M, et al. Resistive switching properties of Au/ZrO2/Ag structure for low-voltage nonvolatile memory applications. IEEE Electron Device Letters 2009; 31(2): 117–119. doi: 10.1109/LED.2009.2036276
3. Napolean A, Sivamangai NM, Rajesh S, et al. Review on role of nanoscale HfO2 switching material in resistive random access memory device. Emergent Materials 2022; 5: 489–508. doi: 10.1007/s42247-022-00356-0
4. Lee SY, Chang J, Choi J, et al. Investigation of ultrathin Pt/ZrO2–Al2O3–ZrO2/TiN DRAM capacitors Schottky barrier height by internal photoemission spectroscopy. Current Applied Physics 2017; 17(2): 267–271. doi:10.1016/j.cap.2016.12.004
5. Wang ZJ, Bai Y. Resistive switching behavior in ferroelectric heterostructures. Small 2019; 15(32): 1805088 doi:10.1002/smll.201805088
6. Kim S, Jeong HY, Choi SY, Choi YK. Comprehensive modeling of resistive switching in the Al/TiOx/TiO2/Al heterostructure based on space-charge-limited conduction. Applied Physics Letters 2010; 97(3): 033508. doi:10.1063/1.3467461
7. Wang Z, Wu H, Burr GW, et al. Resistive switching materials for information processing. Nature Reviews Materials 2020; 5(3): 173–195. doi: 10.1038/s41578-019-0159-3

8. Ielmini D. Resistive switching memories based on metal oxides: Mechanisms, reliability and scaling. Semiconductor Science and Technology 2016; 31(6): 063002. doi: 10.1088/0268-1242/31/6/063002
9. Xiao Z, Kisslinger K, Chance S, et al. Comparison of hafnium dioxide and zirconium dioxide grown by plasma-enhanced atomic layer deposition for the application of electronic materials. Crystals 2020; 10(2): 136. doi:10.3390/cryst10020136
10. Li Y, Long S, Lv H, et al. Improvement of resistive switching characteristics in ZrO2 film by embedding a thin TiOx layer. Nanotechnology 2011; 22(25): 254028. doi: 10.1088/0957-4484/22/25/254028
11. Wu Z, Zhu J, Zhou Y, Liu X. Bipolar resistive switching properties of Hf0.5Zr0.5O2 thin film for flexible memory applications. Physica Status Solidi (A) 2018; 215(1): 1700396. doi: 10.1002/pssa.201700396
12. Ryu SW, Cho S, Park J, et al. Effects of ZrO2 doping on HfO2 resistive switching memory characteristics. Applied Physics Letters 2014; 105(7): 072102. doi: 10.1063/1.4893568
13. Huang CY, Huang CY, Tsai TL, et al. Switching mechanism of double forming process phenomenon in ZrOx/HfOy bilayer resistive switching memory structure with large endurance. Applied Physics Letters 2014;104(6): 062901. doi: 10.1063/1.4864396
14. Yan X, Xiao Z, Lu C. Characteristic investigation of highly oriented Hf0.5Zr0.5O2 thin-film resistive memory devices. Applied Physics Letters 2020; 116(1): 013506. doi: 10.1063/1.5141132
15. Sekhar Reddy PR, Janardhanam V, Rajagopal Reddy V, et al. Effects of rapid thermal annealing on the structural, optical, and electrical properties of Au/CuPc/n-Si (MPS)-type Schottky barrier diodes. Applied Physics A 2021; 127(10): 803. doi: 10.1007/s00339-021-04945-4
16. Mikhaylov AN, Belov AI, Guseinov DV, et al. Bipolar resistive switching and charge transport in silicon oxide memristor. Materials Science and Engineering: B 2015; 194: 48–54. doi: 10.1016/j.mseb.2014.12.029
17. Lim EW, Ismail R. Conduction mechanism of valence change resistive switching memory: A survey. Electronics 2015; 4(3): 586–613. doi: 10.3390/electronics4030586
18. Yuan FY, Deng N, Shih CC, et al. Conduction mechanism and improved endurance in HfO2-based RRAM with nitridation treatment. Nanoscale Research Letters 2017; 12(1): 574. doi: 10.1186/s11671-017-2330-3
19. Sekhar Reddy PR, Nallagatla VR, Kumar YA, Murali G. Enhanced resistive switching properties of HfAlOx/ZrO2-based RRAM devices. Progress in Natural Science: Materials International 2022; 32(5): 602–607. doi:10.1016/j.pnsc.2022.09.013