High-performance bilayer flexible resistive random access memory based on low-temperature thermal atomic layer deposition

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Abstract
We demonstrated a flexible resistive random access memory device through a low-temperature atomic layer deposition process. The device is composed of an HfO2/Al2O3-based functional stack on an indium tin oxide-coated polyethylene terephthalate substrate. After the initial reset operation, the device exhibits a typical bipolar, reliable, and reproducible resistive switching behavior. After a 10^4-s retention time, the memory window of the device is still in accordance with excellent thermal stability, and a 10-year usage is still possible with the resistance ratio larger than 10 at room temperature and at 85°C. In addition, the operation speed of the device was estimated to be 500 ns for the reset operation and 800 ns for the set operation, which is fast enough for the usage of the memories in flexible circuits. Considering the excellent performance of the device fabricated by low-temperature atomic layer deposition, the process may promote the potential applications of oxide-based resistive random access memory in flexible integrated circuits.

Keywords: Flexible memory, Atomic layer deposition, Low temperature

Background
Since flexible electronic system (FES) appeals to be light, convenient, has conformal contingency with the crooked surface, and excellent interfaces with humans, it ought to be a prospective existing form of electronic product to substitute its clumsy predecessors manufactured and packaged by traditional bulk silicon technology [1,2]. Up to now, multifarious electronic components, such as integrated circuits (ICs) [3,4], active matrix organic light-emitting diodes [5], sensors [6], radiofrequency identification antennas [7], and solar cells [8,9], have been fabricated on flexible substrates and are delved by many researchers. As we know, among all the components used in ICs, good and reliable memories [10,11] will maximize the functionality of ICs, and it is also important for the FES.

Among all the memories, nonvolatile resistive random access memory (RRAM) is the most promising candidate because of its low power consumption, high speed, simple structure, and high packaging density, compared with its counterparts such as flash memory and DRAM [12-14]. Currently, oxides, such as STO [15], HfO2 [16], NiO [17], Al2O3 [18], ZnO [19], and GO [20], have received much interest in resistive switching research. Among the oxides mentioned, HfO2 has been profoundly studied and contains great potentiality to be put into applications. However, the application of HfO2-based RRAM on flexible substrate is still rare.

In recent years, atomic layer deposition (ALD) has emerged as a new technique for depositing films, particularly for fabricating oxide films. Owing to its self-limiting mechanism during the process, excellent step coverage and conformal thickness of the film can be achieved [21]. Although the deposition of oxide film by ALD on bulk silicon is very mature, seldom had researchers used this method to deposit films on flexible substrate. The main reason is that the flexible substrate could not undergo high-temperature processing above 200°C, except in some cases such as depositing films using plasma-enhanced atomic layer deposition under low temperature where plasma damage and degradation of the step coverage is unavoidable [22].
In this letter, we fabricated a bilayer flexible RRAM device based on HfO$_2$/Al$_2$O$_3$ films under low temperature, with resistive layers deposited using a low-temperature ALD process at 120°C and the electrodes sputtered by direct current (DC) magnetron reactive sputtering at room temperature. The devices fabricated by these methods exhibit impressive resistive switching characteristics with reliable data retention properties under room temperature and elevated temperature up to 85°C.

**Methods**

Flexible RRAM was fabricated on polyethylene terephthalate (PET) substrate coated by indium tin oxide (ITO) conducting film, and ITO serves as the bottom electrode in our devices. During the process, the substrate was fixed on a 3-in wafer with polyimide tapes in order to maintain sufficient mechanical support. The Al$_2$O$_3$ layer was deposited by 41 cycles of low-temperature ALD at 120°C with trimethyl aluminum (TMA) and water.
as precursors. Subsequently, the HfO2 layer was deposited by 67 cycles within the same framework using tetrais(ethylmethylamino)hafnium (TEMAH) and water as precursors. TMA was pulsed at room temperature, and TEMAH was heated to 85°C to offer enough evaporation pressure. Al2O3 film was deposited with a pulse time of 0.1 and 0.2 s for TMA and water, and the purging time for TMA and water was 5 and 20 s, respectively. The deposition method of HfO2 was derived from our previous work [23]. Finally, a 50-nm TiN top electrode was sputtered on the resistive layer by DC magnetron reactive sputtering through a metal shadow mask with a diameter of 400 μm.

The thicknesses of the HfO2 and the Al2O3 layer were estimated to be 10.1 and 4.9 nm by Sopra GES5E spectroscopic ellipsometry. X-ray photoelectron spectroscopy (XPS) of HfO2 and Al2O3 on the PET substrate was performed using a Kratos Axis Ultra DLD XPS (Kratos Analytical, Ltd., Manchester, UK). Electrical properties at room temperature and at 85°C of the device were assayed using an Agilent B1500A (Agilent Technologies, Inc., Santa Clara, CA, USA) semiconductor parameter analyzer and an Agilent B1525A high-voltage semiconductor pulse generator. Impedance of high and low resistance states was analyzed by an Agilent 4294A precision impedance analyzer. The device was tested with top biased and grounded bottom electrodes.

Results and discussion

The XPS spectra of HfO2 and Al2O3 films are respectively shown in Figure 1a,b. In Figure 1a, the binding energies of Al 2p in the bulk and at the surface of the Al2O3 film are both at 73.9 eV, and the binding energies of O 1s in the bulk and at surface of the Al2O3 film show that the Al-O bond is at about 530.8 eV without any shifts. In Figure 1b, the bulk and surface XPS spectra of the HfO2 film illustrate that the binding energies of the Hf 4f5/2 and 4f7/2 are at the positions of about 18.4 and 16.7 eV, respectively, with a 1.7-eV spin-orbit splitting. From the O 1s spectrum in Figure 1b, the Hf-O bond is at 530 eV in the interior and at the surface of the HfO2 film [24]. However, from the surface XPS of O 1s in both Al2O3 and HfO2, the existence of -OH is observed with a peak at around 532 eV. This is either incorporated by residue water precursors during the process because of the high desorption energy of water at low temperatures or exposing the film to the atmosphere (CO2 and moisture) before XPS measurement [23]. The XPS qualification report shows that the ratios of the O/Al in the bulk of the Al2O3 film and the O/Hf in the bulk of the HfO2 are about 1.7 and 2, respectively, which means that our films obtained at low temperature are almost stoichiometric.

Typical I-V characteristics of the device are shown in Figure 2, which indicates a bipolar resistive switching. The initial resistance state of the TiN/HfO2/Al2O3/ITO flexible RRAM (schematically shown in the inset of Figure 2) device was found (curve 1) to be even lower than the low resistance state (LRS) of the device, and an excess negative voltage was applied to reset the device to high resistance state (HRS). The initial reset voltage and current were −3 V and 10 mA, respectively. This phenomenon was not observed in RRAMs grown at high temperatures, except in some cases after high-temperature annealing [25-27]. We attribute this phenomenon to the high density of defects in the film grown at low temperature. As with our low-temperature ALD processing using H2O as oxidant, it is inevitable that there will be some incomplete reactions during the process, such as residual -OH groups, fixed positive charges, and oxygen vacancies. It is considered that when the density of defects exceeds the percolation theory threshold value, the resistance of the insulating layer will be lower than the typical value [26,28]. This large density of defects may be very suitable for RRAM applications which work dependently on the defects. After the initial reset operation, the set operation was achieved by sweeping a positive voltage from 0 to 1.5 V with 1 mA of current compliance to protect the device from a hard breakdown (curve 3). An abrupt increase of current was observed at 1 V, and the device was set to LRS (approximately 650 Ω). A negative bias was then applied to the device by a sweep from 0 to −1 V, and a sudden descent of current occurred at −0.6 V, indicating that the device was reset to HRS with a reset current in the same magnitude as the set current.

To further investigate the conduction mechanism in the flexible RRAM, the I-V states were re-plotted in a dual logarithmic plot. As shown in Figure 3a, the logarithmic plot and linear fitting of the previous I-V curve for the device in LRS show
a typical ohmic conduction with a slope of 0.95, which is considered to be the formation of conductive filaments in the memory cell during the set process. On the other hand, the conduction mechanism of the device in HRS seems to be more complicated, with considerable disparities in negative and positive sweepings. The fitting result for the device in HRS under negative bias is presented in Figure 3b, and the slopes of the curve differ from each other under different voltages. When the electric field is small, the I-V slope is about 1.08, which conforms to ohmic conduction. However, when the voltage enters into the high electric field, the relationship between logarithm voltage and logarithm current turns to be an \( aV^2 + bV \) relation, which is the classical space charge-limited conduction (SCLC). However, for the conduction behavior of the OFF state in devices under positive bias (Figure 3c), the slope is estimated to be 1.27 when the electric field is small, and the slope raises to 3.77 when the electric field is large enough until it approaches the compliance current (1 mA). As it is widely accepted that in oxide-based films the electron hops across the film through the body oxygen vacancies or defects, we attribute the conduction mechanism for the device in HRS under positive bias to be the trap-assisted tunneling (TAT) conduction \[29\]. When a negative bias was applied on the device, electrons are injected from the top electrode (TE) to the oxide and then proceed to the bottom electrode (BE). The resistance of TE to oxide is much larger than that of oxide to BE. As a result, the current is limited by the available electron in the oxide and leads to SCLC conduction. On the other hand, when a positive voltage was applied on the device, electrons are injected from BE to the oxide and then proceed to the TE. The current is limited by the traps available in the oxide near TE. As a result, the conduction mechanism will possibly be TAT.

Figure 4 shows the data retention characteristics of the flexible RRAM device at room temperature and under high temperature up to 85°C. Both HRS and LRS were read at 0.1 V for 10^4 s, and a predetermination of the long-term retention was made. At room temperature, no significant degradation of the memory window was

![Figure 3](image3.png)

**Figure 3** Dual logarithmic plots of the current–voltage characteristics. (a) ON state device, (b) OFF state device under negative bias, and (c) OFF state device under positive bias.

![Figure 4](image4.png)

**Figure 4** Read disturbance test for device after 10^4 s retention time under room temperature and at 85°C. No significant degradation of resistance ratio was observed under room temperature, and there is a slightly parallel descent of the HRS and LRS at 85°C.
observed, with the HRS ascending slightly. It suggests that sufficient memory margin still exists when the device undergoes decade employment. At elevated temperature (85°C), even with descents of both LRS and HRS, the memory window is still in accordance with excellent thermal stability, and a 10-year usage is still possible, with the resistance ratio larger than 10.

The speed of the set and reset operations with different pulse widths at ±5 V is exhibited in Figure 5, and the resistance state of the device after the pulse was read at 0.1 V. We found that the resistive switching phenomenon occurs when the pulse width is larger than 500 ns for reset operation and 800 ns for set operation. The operation speed of the memory cell is a little faster than some cases before [22,30].

Stable and reproducible switching characteristics have been displayed in Figure 6 with a consistent 400 switching cycle without failures by DC sweeping. The sweeping voltage was applied from 0 to 2 V for set and 0 to −2 V for reset with a reading voltage of 0.1 V at room temperature. In Figure 6a, the result of the endurance test shows that memory ratio remains above 10:1 all along. Furthermore, statistics of the resistances and operation voltages are conducted separately according to the endurance test result. The resistance distributions of the LRS and HRS have been shown in Figure 6b, and we can find that only a small dispersion, with almost 90% of the LRS around 0.6 kΩ and 80% of the HRS around 10 kΩ, existed during the switching. In addition, Figure 6c shows the operation voltage distributions for set and reset. It can be obviously observed that almost 99% of the reset voltages are near −2 V and almost 85% of the set voltages are around 1 V. Through all the statistical results and previous test result, we can conclude that
our flexible RRAM is characterized with high uniformity and reliability.

To inspect the equivalent circuit model of the device, we measured the impedance of the device in HRS and LRS in the Z-Z (θ) mode by applying 20 mV of AC small signal (40 Hz to 110 MHz) to the device. Figure 7 shows the Nyquist plot ($Z''-Z', Z''$, and $Z'$ represent the absolute value of imaginary parts and real parts of the impedance) of the device in the LRS and HRS. In Figure 7a, one semicircle is observed in the LRS, indicating the equivalent RC parallel circuit model. Parameters from the fitting results reveal the existence of a tiny capacitance and a big resistance, which is in consonance with the conductive filament (CF) theory that when the RRAM is in LRS, it is mainly a resistance formed by the CF [10]. On the other hand, the calculated parameters for the HRS are shown in the inset of Figure 7b, and the device exhibits two different semicircles which indicate the complex equivalent circuit model that contains two RC parallel sections in series. In the LRS of the device, conducting filaments are formed in the device, and as a result, the device can be considered as a resistor with small resistance and a capacitor (the area without formed filaments) with small capacitance. On the other hand, when the device is in HRS, conducting filaments are ruptured at a certain position in the oxide. The ruptured place will induce an additional tunneling resistor with big resistance and a capacitor with big capacitance.

Conclusions

In conclusion, a highly reliable and uniform flexible RRAM based on the TiN/HfO$_2$/Al$_2$O$_3$/ITO structure, fabricated by a low-temperature process, was investigated. The fresh cell shows an ultra-low resistance state, and after the initial reset operation, a typical bipolar reliable and reproducible resistive switching behavior was demonstrated. It is found that the memory window is still in accordance with excellent thermal stability after a 10$^4$s retention time, and a 10-year usage is still possible with the resistance ratio larger than 10 at room temperature and at 85°C. The resistance of the LRS and HRS exhibits a very concentrated distribution with almost 90% of the LRS around 0.6 kΩ and 80% of the HRS around 10 kΩ. The developed low-temperature process for the memories may promote the potential applications of oxide-based RRAM in flexible ICs.

Competing interests

The authors declare that they have no competing interests.

Authors’ contributions

RCF carried out the sample fabrication and drafted the manuscript. WY carried out the device measurements. PZ and PFW participated in writing the manuscript and in the discussion of results. QQS and DWZ participated in the design of the study and performed statistical analysis. All authors read and approved the final manuscript.

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References
1. Reuss RH, Chalamala BR, Moussessian A, Kane MG, Kumar A, Zhang DC, Rogers JA, Hatalis M, Temple D, Moddel G, Elssion BJ, Estes MI, Kunze J, Handl ES, Harmon ES, Salzman P, Woodall JM, Alam MA, Murphy JY, Jacobsen SC, Olivier M, Markus D, Campbell PM, Snow E. Macroelectronics: perspectives on technology and applications. Proc IEEE 2005, 93:1239–1256.
2. Tsutui T, Fujita K. The shift from “hard” to “soft” electronics. Adv Mater 2002, 14:549–552.
3. Cao G, Kim HS, Pimparkin N, Kulkarni JP, Wang CJ, Shim M, Roy K, Alam MA, Rogers JA. Medium-scale carbon nanotube thin-film integrated circuits on flexible plastic substrates. Nature 2008, 454:495–500.
4. Kim MG, Kanatzidis MG, Facchetti A, Marks TJ. Low-temperature fabrication of high-performance metal oxide thin-film electronics via combustion processing. Nat Mater 2011, 10:382–388.
5. Li JF, Hu LB, Liu J, Wang L, Marks TH, George G. Indium tin oxide modified transparent nanotube thin films as effective anodes for flexible organic light-emitting diodes. Appl Phys Lett 2008, 923:083306.
6. Kuniharu T, Toshitake T, Johnny CH, Hyunhyub K, Andrew GG, Paul WL, Ronald AF, Ali J. Nanowire active-matrix circuitry for low-voltage macroscopic macroscopic skin. Nat Mater 2010, 9:821–826.
7. Rutherford C, Jan D, Burke P. Nanotube electronics for radiofrequency applications. Nat Nanotechnol 2009, 4:811–819.
8. Kaltenbrunner M, White MS, Glowacki ED, Sekitani T, Somaey T, Sarchihti NS, Bauer S. Ultrathin and lightweight organic solar cells with high flexibility. Nat Commun 2012, 3:1–7.
9. Galiyani V, Vomiero A, Concina I, Braga A, Briscotto B, Bonteremi E, Foglia G, Steinhäuser G. Vertically aligned TiO2 nanotubes on plastic substrates for flexible solar cells. Small 2011, 7:2437–2442.
10. Waser R, Dittmann R, Staikov G, Sotz K. Redox-based resistive switching memories—nanionic mechanisms, prospects, and challenges. Adv Mater 2009, 21:2623–2632.
11. Smukov DB, Snider GS, Steer WD, Williams RS. The missing memristor found. Nature 2008, 453:80–83.
12. Sheu SS, Cheng KH, Chang MF, Chiang PC, Lin WP, Lee HY, Chen PS, Chen YS, Wu TY, Chen FT, Su KL, Kao MJ, Tsai MJ. Fast-write resistive RAM (RRAM) for embedded applications. IEEE Design & Test of Computers 2011, 28:64–71.
13. Tseng YH, Huang CE, Kuo CH, Chih YD, King YC, Lin CJ. A new high-density and ultrasmall-cell-size contact RRAM (CR-RRAM) with fully CMOS-logic-compatible technology and circuits. IEEE Trans Electron Dev 2011, 58:53–58.
14. Sava A. Resistive switching in transition metal oxides. Mater Today 2008, 11:28–36.
15. Sotz K, Speier W, Bihlmayer G, Waser R. Switching the electrical resistance of individual dislocations in single-crystalline SrTiO3. Nat Mater 2006, 5:312–320.
16. Chen YS, Lee HY, Chen PS, Tsai CH, Gu PY, Wu TY, Tsai KH, Sheu SS, Lin WP, Lin CH, Chiu PF, Chen WS, Chen FT, Lien C, Tsai MJ. Challenges and opportunities for HfO2-based resistive random access memory. In IEEE International Electron Devices Meeting: 5–7 Dec. 2011. Washington DC: IEEE; 2011:31.1–31.4.
17. Sun QQ, Gu JI, Chen L, Zhou P, Wang PF, Ding SJ, Zhang DW. Controllable filament with electric field engineering for resistive switching uniformity. IEEE Electron Device Lett 2011, 32:1167–1169.
18. Chen L, Xu Y, Sun QQ, Liu H, Gu JI, Ding SJ, Zhang DW. Highly uniform bipolar resistive switching with Al2O3 buffer layer in robust NbAlO-based RRAM. IEEE Electron Device Lett 2010, 31:356–358.
19. Chang WY, Lai YC, Wu TB, Wang SF, Chen F, Tsai MJ. Unipolar resistive switching characteristics of ZnO thin films for nonvolatile memory applications. Appl Phys Lett 2008, 92:022110.
20. Wang LH, Yang W, Sun QQ, Zhou P, Lu HL, Ding SJ, Zhang DW. The mechanism of the asymmetric SET and RESET speed of graphene oxide based flexible resistive switching memories. Appl Phys Lett 2012, 100:063507.
21. George SM. Atomic layer deposition: an overview. Chem Rev 2010, 110:111–131.
22. Kim SJ, Kim SK, Jeong HY. Flexible memristive memory array on plastic substrates. Nano Lett 2011, 11:5438–5442.
23. Fang RC, Wang L, Yang W, Sun QQ, Zhou P, Wang PF, Ding SJ, Zhang DW. Resistive switching of HfO2-based flexible memories fabricated by low temperature atomic layer deposition. J Vac Sci Technol B 2012, 30:020602.
24. Moulder JF, Stickle WF, Sobol PE, Bommen KD, Chastain L. Handbook of X-ray Photoelectron Spectroscopy. Eden Prairie: Perkin Elmer; 1992.
25. Son JY, Kim CH, Cho JH, Shin YH, Jang HM. Self-formed exchange bias of switchable conducting filaments in NiO resistive random access memory capacitors. ACS Nano 2010, 4:5288–5292.
26. Chen YS, Lee HY, Chen PS, Wu TY, Wang CC, Tseng PJ, Chen F, Tsai MJ, Lien C. An ultrathin forming-free HfO2 resistance memory with excellent electrical performance. IEEE Electron Device Lett 2010, 31:1473–1475.
27. Chen WC, Chen YC, Lee FM, Lin YL, Lai EK, Yao YD, Gong J, Horng SF, Yeh CW, Tsai SC, Lee CH, Huang YK, Chen CF, Kao HF, Shih YH, Hsieh KY, Lu CF: A novel Ni/WO3-W resistive random access memory with excellent retention and low switching current. Jpn J Appl Phys 2011, 50:04DD11.
28. Zhao CZ, Zhang JF, Zahid MB, Efthymiou E, Lu Y, Hall S, Peaker AR, Greesenegek N, Pantiso D, Degrave R, Gendt SD, Heyns M. Hydrogen induced positive charge in Hf-based dielectrics. Microelectronic Engineering 2007, 84:2334–2337.
29. Yu SM, Guan XM, Wong HS. Conduction mechanism of TiN/HfO2/Pt resistive switching memory: a trap-assisted-tunneling model. Appl Phys Lett 2011, 99:063507.
30. Jeong HY, Kim YI, Choi SY. A low-temperature-grown TiO2-based device for the flexible stacked RRAM application. Nanotechnology 2010, 21:15203.

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