Enhanced Ga$_2$O$_3$-Based RRAM via Stacked Bilayer ZnO/Ga$_2$O$_3$

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The stability and endurance of resistive random-access memory (RRAM) devices over long-term use has been widely acknowledged as a concern. Therefore, different top electrodes and oxygen concentration flows were used with stacked ZnO/Ga$_2$O$_3$ as the switching layer to enhance the performance of Ga$_2$O$_3$-based RRAM. All switching layers were deposited by radio frequency sputtering in this study, and the oxygen vacancies were well controlled by controlling the oxygen concentration flow. When a stacked structure was formed, the gradients in the concentration of oxygen vacancies and mobility influenced the set and reset processes. With the stacked structure, the average set voltage was 1.5 V, and the average reset voltage was ~0.7 V. In addition, under DC sweeps, the stacked RRAM demonstrated a high operating life of more than 300 cycles. In conclusion, the performance and stability of RRAM can be enhanced by adjusting the concentration of oxygen vacancies using different compositions of elements.

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Results and Discussion

Recently, traditional random-access memory (RAM) technologies, such as dynamic RAM, static RAM, and flash memory, have not kept pace with the development of computer science to provide a sufficiently large capacity for data calculation as technologies change rapidly. The challenges faced by traditional RAM technologies are scaling down and improving performance. Therefore, the next generation of memory elements has unlimited potential for achieving the desired advantages. Thus, magnetic RAM, phase change memory, and resistive random-access memory (RRAM) are the most promising candidates. RRAM devices have attracted significant interest because of such advantages as high integration density, high operation density, and simple metal–insulator–metal or metal–semiconductor–metal structures.1–3

Many switching layer materials have been reported for RRAM devices, including transition metal oxides and rare-earth element oxides. Gallium oxide (Ga$_2$O$_3$) has been widely used in academia owing to its advantages, such as an ultrawide bandgap of 4.8 eV, high thermal stability, and potential for mass production. In addition, it has an inherently high resistance and very sensitive conductivity to oxygen, which leads to a high on/off ratio. However, the challenge of poor endurance must be addressed.

Oxygen vacancies in the switching layer are arranged by the applied voltage and form conductive filaments; in other words, oxygen vacancies play an important role in resistive switching. Moreover, several studies have indicated that different top electrodes (TEs) may interact with the switching layer and affect performance.3,9 Considering the above concerns, different oxygen flows of single-layer Ga$_2$O$_3$ with three different TEs (Al, Ti, and Pt) were fabricated and investigated in this study. To improve the endurance, ZnO was stacked on Ga$_2$O$_3$ to create a native gradient of oxygen vacancy concentration. Because ZnO has inherently more-abundant oxygen vacancies than Ga$_2$O$_3$, it is believed that the switching behavior can become more stable with the aid of a native concentration gradient caused by the stacked structure.

Experimental

Four RRAM devices with different switching layers, three single-layer RRAM with different TEs (Al, Ti, and Pt), and a bilayer ZnO/Ga$_2$O$_3$ RRAM with an Al TE were fabricated. First, borosilicate glass substrates were cleaned with acetone, isopropyl alcohol, and deionized water in an ultrasonic oscillator for 5 min each. A 10-nm-thick Ti layer was deposited on the cleaned glass as an adhesion layer using an electron-beam evaporator. Then, 50 nm of Pt was deposited on the adhesion layer as the bottom electrode (BE) using an electron-beam evaporator. In the single-layer RRAM, Ga$_2$O$_3$ deposition was performed by radio frequency (RF) magnetron sputtering with various Ar/O$_2$ gas flows and a thickness of 30 nm. The ambient pressure, growth pressure, and RF power for the Ga$_2$O$_3$ target were, respectively, 5 × 10$^{-6}$ Torr, 5 mTorr, and 80 W. The Ar/O$_2$ gas flow was controlled at 50/0 sccm (0%), 45/5 sccm (10%), and 40/10 sccm (20%). Finally, Al, Ti, and Pt were deposited as the BE by thermal evaporation of Al using an electron-beam evaporator.

In the bilayer RRAM, 15-nm-thick Ga$_2$O$_3$ with Ar/O$_2 = 50/0$ was deposited under the same conditions in a single layer, and then 15 nm of ZnO with Ar/O$_2 = 50/0$ was deposited under the same conditions in a single layer. Finally, Al was deposited as the BE by thermal evaporation. The patterns were defined by a shadow mask of 50 × 50 μm for the TE and 1500 × 1500 μm for the active layer. The electrical properties of the devices were measured using a two-point probe with a B1500/A semiconductor parameter analyzer (Agilent, Santa Clara, CA, USA), and the BE was grounded. A schematic diagram of the RRAM is shown in Fig. 1.

**Figure 2** shows the endurance tests of a single Ga$_2$O$_3$ layer with Al and Ti TEs. The results indicate that, with an increase in the oxygen concentration ratio, the on/off ratio and endurance performance decreased. This may be because, as the oxygen concentration ratio increased, the number of oxygen vacancies decreased. Therefore, the distribution of oxygen vacancies in the filament was more concentrated, and the set voltage and on/off ratio were slightly lower because of the easily formed filament. However, a variation followed. In addition, with the Ti TE, there was a gradual degradation in the switching process. **Figure 3** shows the set/reset voltages of a single Ga$_2$O$_3$ layer with Al and Ti TEs. The set/reset voltages of the Al TE with oxygen concentration ratios of 0%, 10%, and 20% were 5.3/−0.6, 4.8/−0.7, and 4.5/−0.6 V, and those of the Ti TE were 2.8/−1.4, 1.8/−1.3, and 3.3/−0.8 V, respectively (Table I). **Figure 4** shows the I–$V$ curve of the single Ga$_2$O$_3$ layer with the Pt TE, which reveals no resistive switching. Therefore, an oxygen concentration ratio of 0% and an Al TE were chosen for the bilayer ZnO/Ga$_2$O$_3$ RRAM because of its good on/off ratio, satisfactory endurance, and lack of gradual degradation.

**Figure 5** shows bilayer ZnO/Ga$_2$O$_3$ characteristics of (a) I–$V$ curve, (b) endurance, (c) set/reset voltage, and (d) retention. The endurance indicates that the bilayer ZnO/Ga$_2$O$_3$ RRAM can operate...
under a DC sweep of more than 300 cycles, an on/off ratio of more than 10^3, and a set/reset voltage of 1.5/−0.7 V. The retention is more than 10 ks. Moreover, Fig. 6 shows that, for the high resistance state/low resistance state (HRS/LRS) resistance and set/reset voltage, the bilayer RRAM has less variation than the single-layer one.

Figure 7a shows a cross-sectional image of the bilayer ZnO/Ga2O3 RRAM obtained using a transmission electron microscope. The total thickness of the switching layer was approximately 32 nm, and a significant interface was observed between the two ZnO/Ga2O3 layers. The Zn content decreased, and the Ga content increased from the TE to the BE, as shown in Fig. 7b. The transmission electron microscopy (TEM) results indicate that the thickness and elements of the fabricated ZnO/Ga2O3 bilayer RRAM were well controlled.

From the X-ray photoelectron spectroscopy (XPS) results, the O 1s peak can be deconvoluted into three peaks at 530.1, 531.9, and 532.3 eV through Gaussian fitting. The peak at 530.1 eV is assigned to the well-bonded oxygen with the metal cation (M−O), the peak at 531.9 eV is assigned to the oxygen vacancies (V_O), and the peak at 532.3 eV is assigned to the hydroxy(−OH) group. By calculating the ratio of the area below the curve representing V_O to the total area below the O 1s curve, the number of oxygen vacancies in the Ga2O3 and ZnO layers can be extracted. As shown in Fig. 8, the number of oxygen vacancies decreased by 20%, 19.5%, and 18.4% when the oxygen concentration ratio increased with values of 0%, 10%, and 20% in the Ga2O3 layer. The number of oxygen vacancies in the ZnO was the highest, with a value of 27.3%.

As Fig. 9 shows, when a positive bias is applied on the TE, the oxygen ion in the oxide moves toward the TE and leaves an oxygen vacancy behind, and the oxygen vacancy is arranged to form a conductive filament (this is the set process). Two main mechanisms affect the filament during the reset process. When a negative bias is applied to the TE, the Coulombic force causes the oxygen ion to move back to recombine with the oxygen vacancy and block the conductive filaments, which is the oxidation−reduction (redox) reaction domination. Because of the Joule heat effect, a large current makes the oxygen vacancy disordered in the filament owing to the current crowding effect. This process is irreversible, and thus the path of the filament becomes different. If the reset process is dominated by the Joule heat effect, the maximum reset current...
would be much larger than the maximum set current, which would critically affect the stability. On the contrary, if the reset process is dominated by the redox reaction, the maximum set current would be almost the same as the maximum reset current because the reaction is reversible, as shown by the $I$–$V$ curve in Fig. 10. Figures 2d–f show that there is a degradation in the Ti TE, and some studies have indicated the overgrowth of conductive filaments. The formation of an electrode interfacial oxide layer induced by the anode oxidation effect during the forming/set process dominates the endurance degradation, which blocks the electron and oxygen ion transportation. Thus, in the reset process, the conductive filaments are not destroyed completely. In the set process, the conductive filaments are not formed completely. This is the reason for the increased RLRS and reduced RHRS.

For the bilayer ZnO/Ga2O3 RRAM, in addition to the redox reaction domination reset process, there is a gradient in the concentration of oxygen vacancies, as shown in the XPS analysis in Fig. 8. This implies that the bilayer RRAM requires only a small electric field to arrange the oxygen vacancies and form a conductive filament. The binding energy of Zn–O is lower than that of Ga–O, so oxygen ions can migrate more easily in ZnO, which implies that it helps oxygen migration during the set/reset process. Therefore, its set voltage is much lower (1.5 V), it is more stable than a single layer, and its endurance is greater than that of the single layer.11

Figure 3. Set/reset voltages with Al TEs of oxygen concentration ratios of (a) 0%, (b) 10%, and (c) 20% and with Ti TEs of oxygen concentration ratios of (d) 0%, (e) 10%, and (f) 20%.

Table I. Extracted electrical parameters of the fabricated Ga2O3-based RRAM devices with different oxygen concentration flows and TEs.

| TE  | Switching layer | Set voltage (V) | Reset voltage (V) | On/off ratio | Cycles |
|-----|-----------------|-----------------|-------------------|--------------|--------|
| Al  | Ga2O3, 0%       | 5.3             | −0.6              | $>10^7$      | 131    |
| Ti  |                 | 2.8             | −1.4              | $>10^5$      | 132    |
| Al  | Ga2O3, 10%      | 4.8             | −0.7              | $>10^3$      | 94     |
| Ti  |                 | 1.8             | −1.3              | $>10^5$      | 146    |
| Al  | Ga2O3, 20%      | 4.5             | −0.6              | $>10^3$      | 237    |
| Ti  |                 | 3.3             | −0.8              | $>10^3$      | 50     |
| Al  | ZnO/Ga2O3       | 1.5             | −0.7              | $>10^3$      | 347    |

Figure 4. $I$–$V$ curve of Pt TE.
Figure 5. Bilayer ZnO/Ga₂O₃ characteristics of (a) I–V curve, (b) endurance, (c) set/reset voltage, and (d) retention.

Figure 6. Cumulative resistance of (a) single-layer Al/Ga₂O₃ 0%/Pt and (b) bilayer Al/ZnO/Ga₂O₃/Pt and cumulative set/reset voltage of (c) single-layer Al/Ga₂O₃ 0%/Pt and (d) bilayer Al/ZnO/Ga₂O₃/Pt.
Conclusions

A single-layer Ga₂O₃ RRAM with different oxygen concentration flows of 0%, 10%, and 20% and different TEs of Al, Ti, and Pt was fabricated, as well as a bilayer ZnO/Ga₂O₃ RRAM with an Al TE. Compared with other TEs and oxygen concentration flows, the single-layer Ga₂O₃ RRAM with an oxygen concentration flow of 0% and an Al TE has a better endurance and on/off ratio and no degradation. The bilayer ZnO/Ga₂O₃ RRAM can operate more than 347 times with a smaller average set voltage of 1.5 V than a single layer and with an average reset voltage of −0.7 V, and it is more stable. The improved result is due to the original gradient of the concentration of oxygen vacancies and the mobility of the stacked layers, which stabilize the set and reset processes. Furthermore, the reset process of the stacked ZnO/Ga₂O₃ RRAM is dominated by the reversible redox reaction.

Figure 7. (a) TEM image of the cross-sectional view of the bilayer ZnO/Ga₂O₃ RRAM and (b) TEM-EDS line scan spectrum of the bilayer ZnO/Ga₂O₃ RRAM.

Figure 8. XPS O 1s spectra of (a) Ga₂O₃ 0%, (b) Ga₂O₃ 10%, (c) Ga₂O₃ 20%, and (d) ZnO thin film.
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Figure 9. Schematic diagram illustrating the redox reaction of the (a) set process and (b) reset process.

Figure 10. DC sweep I–V curve of single layer of (a) Al TE with oxygen concentration ratio of 0%, (b) Ti TE with oxygen concentration ratio of 0%, and (c) bilayer RRAM.