# Effect of Oxidation Amount on Gradual Switching Behavior in Reset Transition of $\mathrm{Al} / \mathrm{TiO}_{2}$ based Resistive Switching Memory and its Mechanism for MLC Operation 

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#### Abstract

In order to analyze and explain the gradual reset switching property of the bipolar switching resistive random access memory (RRAM) for MLC operation, the effect of plasma oxidation amount on gradual reset switching behavior of $\mathrm{Al} / \mathrm{TiO}_{2}$ based RRAM cell structure is investigated. The device which experienced plasma oxidation in shorter time has better maximum/minimum current $\left(I_{\text {max }} / I_{\text {min }}\right)$ ratio and shows increased maximum current $\left(I_{\text {max }}\right)$. The device which experienced plasma oxidation in longer time shows occasionally the step reset switching behavior due to the thick conductive filament formation at ON state. This is clearly explained by different conduction mechanism during ON state.

\section*{Introduction}

Among new memory candidates, RRAM has attracted more and more interest due to its possible characteristics of low-cost productivity, high-speed operation, low-power application, and feasibility of high-density integration. In particular, transition metal oxide (TMO) based bipolar resistive switching materials such as $\mathrm{WO}_{\mathrm{x}}, \mathrm{HfO}_{2}, \mathrm{TaO}_{\mathrm{x}}$, and $\mathrm{TiO}_{2}$ have showed multi-level cell (MLC) operation possibility in a simple structure [1-4]. In RRAM, robust and stable MLC operation can be possible by having the large current ratio and gradual reset switching behavior with wide reset current and voltage range. In this paper, in order to analyze and elucidate the gradual reset switching property, the effect of plasma oxidation amount on gradual reset switching behavior of $\mathrm{Al} / \mathrm{TiO}_{2}$ based RRAM cell structure is investigated by using our novel conductive filament (CF) model.


## Experiments

The device was fabricated as a cross-pointed metal-insulator-metal (MIM) cell structure whose cell area is $0.2 \mu \mathrm{~m} \times 0.2 \mu \mathrm{~m}$. Schematic structure and process flow of the fabricated device are shown in Fig. 1(a) and 1(b), respectively. Iridium (Ir) was used for top electrode (TE) and bottom electrode (BE). $\mathrm{O}_{2}$ plasma oxidation time in one cycle is split in order to investigate the effect of oxidation amount. Used oxidation times were 30,60 , and 120 seconds. After the $\mathrm{TiO}_{2}$ layer formation, the aluminum ( Al ) insertion layer was deposited in order to improve the resistive switching operation [5-7]. The thickness of Al insertion layer was 0.8 nm . Figure 1(c) shows TEM image of the fabricated device. All electrical measurements were performed by a conventional two-probe method at room temperature using Agilent 4156C semiconductor parameter analyzer and all bias sweeps were conducted at TE while the BE was grounded. In order to avoid excessive current flow, the compliance current was fixed at 3 mA during the forming and the set process. Figure 2 shows the typical bipolar resistive switching I-V curves of the fabricated devices with different oxidation time. Forming and set transition occur at negative voltage region and reset transition occurs at positive voltage region. In order to investigate the gradual reset switching characteristics, the bias was swept from zero to the $\mathrm{V}_{\mathrm{GR}}$ (above $\mathrm{V}_{\text {reset }}$ ) and $V_{G R}$ was increased by 0.1 V per each sweep as shown in Fig. 3. For example, first sweep was from 0 to the 1.5 V and second sweep was from 0 to the 1.6 V , and so on. The read voltage ( $\mathrm{V}_{\text {read }}$ ) is 0.5 V in this experiment and the read current ( $\mathrm{I}_{\text {read }}$ ) is the current at 0.5 V . $\mathrm{I}_{\text {max }}$ and $\mathrm{I}_{\text {min }}$ are the maximum current and the minimum current among all read currents, respectively. $I_{\text {max }}$ is the set current or the ON current in most cases.

## Results and Discussions

First of all, we investigated the effects of Al insertion layer. Figure 4 indicates the $\mathrm{I}_{\text {max }} / \mathrm{I}_{\text {min }}$ ratio of the control device and the Al inserted device. We observed the increase in $\mathrm{I}_{\text {max }} / \mathrm{I}_{\text {min }}$ ratio in the $\mathrm{Ir}(\mathrm{TE}) / \mathrm{Al} / \mathrm{TiO}_{2} / \mathrm{Ir}(\mathrm{BE})$ structure as compared with the $\mathrm{I}_{\text {max }} / \mathrm{I}_{\text {min }}$ ratio in the $\mathrm{Ir} / \mathrm{TiO}_{2} / \mathrm{Ir}$ structure. Inset of Fig. 4 indicates that the $\mathrm{I}_{\max }$ and $\mathrm{I}_{\text {min }}$ of the Al inserted device are larger than those of the control device. Therefore we checked the pristine resistance before forming process. In Fig. 5, we observed the pristine resistance reduction in Al inserted device. It is thought that this pristine resistance reduction is related to the space charge limited conduction (SCLC) at high voltage regime while control device shows Poole-Frenkel (PF) conduction at high voltage regime as shown in Fig. 6. We think that oxygen vacancies or electron traps are generated in whole $\mathrm{TiO}_{2}$ layer when $\mathrm{Al}_{\mathrm{x}} \mathrm{O}_{\mathrm{y}}$ layer is formed with Al and oxygen between Ir TE and $\mathrm{TiO}_{2}$ interface.

Consequently, the generated oxygen vacancies or electron traps give rise to the increases of $\mathrm{I}_{\max } / \mathrm{I}_{\text {min }}$ ratio and the maximum current level. Figure 7 shows the fitting of I-V curves for understandings of conduction mechanisms of both ON and OFF state of $\mathrm{Al} / \mathrm{TiO}_{2}$ devices. Under negative bias (Fig. 7(a)) and positive bias (Fig. 7(b)), both states show ohmic conduction at low voltage regime and SCLC at high voltage regime. Figure 8(a) shows average and median values of the $I_{\max } / I_{\min }$ ratio of our fabricated device according to the plasma oxidation time. $\mathrm{I}_{\text {max }} / \mathrm{I}_{\text {min }}$ ratio is inversely proportional to the plasma oxidation time and is saturated at about 60 seconds. Figure 8(b) shows the $I_{\max }$ and the $I_{\min }$ of the fabricated device according to the various plasma oxidation time. Comparing Fig. 8(a) with Fig. 8(b), it is manifested that the trend of $\mathrm{I}_{\text {max }} / \mathrm{I}_{\text {min }}$ ratio is due to the trend of $I_{\max }$ while $I_{\min }$ is almost the same. That is, the device which experienced plasma oxidation in the shorter time has better $\mathrm{I}_{\max }$ and $\mathrm{I}_{\max } / \mathrm{I}_{\min }$ ratio. This result indicates that when the oxidation time is short, more oxygen vacancies or electron traps are generated, and then, during the forming process, the generated oxygen vacancies make the CF thicker or increasing in number, and consequently the $I_{\text {max }}$ is increased. Interestingly, the device which experienced plasma oxidation in longer time (in this case, 120 seconds per each cycle) shows various reset switching behaviors as provided in Fig. 9. While Fig. 9(a) shows the typical gradual reset switching curves, Fig. 9(b) shows the step reset switching followed by the current stuck, and Fig. 9(c) shows the step reset switching followed by gradual reset switching. The samples which show the step reset switching behavior as shown in Fig. 9(b) and Fig. 9(c) have larger $I_{\text {max }}$ than that of the sample having gradual reset switching behavior as shown in Fig. 9(a). It is thought that the $I_{\max }$ is increased by the CF which is thicken because the CF is hardly formed during the forming process due to less oxygen vacancy (relatively oxygen-rich $\mathrm{TiO}_{2-\mathrm{x}}$ ). Consequentially, the step reset switching behavior is attributable to the thick CF which is hard to be ruptured while the gradual reset switching occurs in the condition of that there are numerous thin CFs. This can be also explained by the conduction mechanisms of the samples in Fig. 9. While the conduction mechanism of the ON current of the sample in Fig. 9(a) at high voltage shows SCLC (Fig. 10(a)), the conduction mechanism of the ON current of the sample in Fig. 9(c) at high voltage shows ohmic conduction (Fig. 10(b)). It is thought that the relatively thick CF has metallic characteristics and the current through the relatively thick CF flows by ohmic conduction mechanism rather than by SCLC mechanism. Figure 11 provides the schematic pictures elucidating the curves in Fig. 9. Figure 11(a) shows the numbers of the CF leading to the gradual reset switching behavior. Figure 11(b) and 11(c) indicate that the thick CF leads to the step reset switching instead of the gradual reset switching behavior. From the results of Fig. 8, 9 and 10, it is thought that the gradual reset switching behavior is due to the sequential rupturing of the plenty of thin CFs, and in case of the device which has more oxygen vacancies, it is thought that the CF is not formed thickly, but the number of the CF is increased and leads to the gradual reset switching behavior. Therefore, in order to make device be able to operate in MLC mode, the deficient oxygen amount control for large sensing margin should be needed.

## Conclusions

In order to analyze the gradual reset switching property which has been focused for MLC operation of the bipolar switching RRAM, the effect of plasma oxidation amount on the gradual reset switching behavior of $\mathrm{Al} / \mathrm{TiO}_{2}$ based RRAM cell structure is investigated. It is thought that the gradual reset switching is due to the sequential rupturing of the thin CFs. When $\mathrm{TiO}_{2}$ layer has less oxygen amount (more oxygen vacancy amount), the gradual reset switching behavior would be more easily achieved and the increased $I_{\text {max }} / I_{\text {min }}$ ratio would be achieved. Therefore, for the improved MLC operation, the control of the oxygen vacancy amount is crucial. However, by the increased current level, it might also give rise to power consumption problem.

## References

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Fig. 1. (a) Schematic drawing, (b) process flow, and (c) cross-sectional TEM image of our fabricated cell.


Fig. 4. $\mathrm{I}_{\max } / \mathrm{I}_{\text {min }}$ ratio of Al not-inserted and inserted devices. (Inset: $I_{\max }$ and $\mathrm{I}_{\text {min }}$ of devices.)



Fig. 5. Pristine resistance before forming process of Al not-inserted and Al inserted devices.


Fig. 7. I-V curves by log scale (a) under negative bias condition, and (b) under positive bias condition of the fabricated devices.


Fig. 9. Various reset switching behaviors of the samples which experienced plasma oxidation in 120 seconds per each cycle. (a) Typical gradual reset switching curves, (b) the step reset switching behavior followed by the current stuck, and (c) the step reset switching behavior followed by the gradual reset switching.


| Ir |  |  |
| :--- | :--- | :--- |
| AlxOy |  |  |
|  | Thick CF |  |
|  |  |  |
| $\mathrm{TiO}_{2-x}$ |  |  |
|  |  |  |
| Ir |  |  |



Fig. 11. The models elucidating the curves in Fig. 9. (a) The numbers of the CF lead to the gradual reset switching behavior, (b) the thick CF leads to the step reset switching, and (c) the thick CF leads to the step reset switching, and then the remained thin CFs are ruptured sequentially.


Fig. 8. (a) $I_{\text {max }} / I_{\text {min }}$ ratios, and (b) $I_{\max }$ and $I_{\text {min }}$ of the fabricated devices according to oxidation time per each cycle.

Fig. 2. Typical I-V curves of our fabricated devices with various oxidation time.


Fig. 6. (a) I-V curves by $\log$ scale, and (b) $\ln (I / V)$ vs. $V^{1 / 2}$ plot of the fabricated devices before forming.



Fig. 3. The gradual reset switching curve of our fabricated device.

