Switching Mechanism of TaOx ReRAM


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1. Introduction
Recently, various binary oxides [1-5] have been reported for memory applications, but reliability aspects are much less developed. To estimate the reliability characteristics, understanding resistive switching mechanisms is highly demanded. Among various proposed mechanisms, we focused on the redox reaction, since some evidence was obtained in the forming process [1]. According to this mechanism, the stability of the resistance states corresponds to the stability of the redox pair. Generally, the lower the absolute value of the reaction Gibbs energy (AG) of the redox reaction, the lower the reactivity.

In this paper, we report a combined theoretical and experimental study of the resistive switching mechanism. ΔG of various kinds of resistance change materials was calculated. Experimentally we have developed and fabricated special devices to clarify where, and what happened in ReRAM. Data retention results of TaOx agree well with the calculation results.

2. Calculation
We calculated the reaction Gibbs energy (ΔG) for various kinds of resistance change materials. Among these materials, redox pair of TaO5/TaO3 showed the smallest reaction Gibbs energy. A schematic potential energy curve for TaO3 is shown in Fig.1. The redox reaction of TaO can be expressed as

\[ 2\text{TaO}_3 + \text{O}^2- \leftrightarrow \text{Ta}_2\text{O}_5 + 2\text{e}^- \quad (1) \]

This indicates that both the high resistance state (HRS) and the low resistance state (LRS) of TaOx are stable. In other words, TaOx with redox pair of TaO3/TaO5 can be used to realize highly reliable ReRAM.

3. Experiment and Discussion
To investigate where the resistive switching phenomenon takes place in TaOx films, we fabricated the device with 4 electrodes shown in Fig.2(a). Monitoring resistive switching between each terminal concurrently makes it possible to pinpoint the location of the resistance change. As shown in Fig.2(b), by applying negative pulses to electrode A, only the resistances involving electrode B (the region (1), (4) and (6)) changed. This indicates that the resistive switching had taken place locally near electrode B. This result identifies the resistive switching region as being localized at the interface near the anode.

A large area test vehicle was fabricated for clarifying the redox reaction mechanism. As shown in Fig.3(a), the test vehicle contains 100 cells; each cell has an area of \(5 \times 20 \mu\text{m}^2\). After setting the test vehicle to HRS or LRS, the top electrode was thinned to 10 nm. Initial, HRS and LRS test vehicles were examined by Hard X-ray Photoemission Spectroscopy (HX-PES). With this non-destructive experiment technique, we succeeded in observing the Ta 4d bands at the deeply buried interface between anode electrode and TaOx thin film. As shown in Fig.3(b) and Fig.3(c), the ratio of TaO5/βTaO3,5 decreases with a sequence of initial, HRS and LRS, indicating that the TaO3,5 component is reduced to the βTaO3,5 component. These results show the first direct evidence of the redox reaction mechanism.

To enhance the redox reaction in the resistance switching region near the anode, the oxygen profile of the TaOx thin film was controlled by annealing in oxygen ambient. X-ray Photoemission Spectroscopy (XPS) spectra show that the bulk material consists of only TaO3,5, while TaO3,5 appears near the anode, where β and δ mean that the phases are close to TaOx and TaO3,5, respectively (Fig.4).

The optimized Pt/TaOx/Pt memory cell with an area of 0.5 \(\times\) 0.5 \(\mu\text{m}^2\) shows excellent memory properties. The linear trend of log(I)-V1/2 for both HRS and LRS indicates the possibility of Schottky emission (Fig.5). Note that resistive switching is also related to the work function of the electrode, it appears that the Schottky barrier at the Pt/TaOx interface dominates the I-V characteristics.

According to the electric properties and the physical analysis results, the resistive switching occurs on modulation of the barrier height between the anode and TaOx caused by the redox reaction (Fig.6). The interface layer between the anode and bulk TaOx includes TaO3,5 and TaO3,5. For a reset operation, by applying the positive voltage pulse on the anode electrode, O2+ ions migrate from the bulk TaOx, which is assumed as an oxygen reservoir, and accumulate around the anode. Then the oxidation reaction of the TaO3,5 and O2 leads to the formation of the TaO3,5 according to the reaction formula (1). Increasing of the TaO3,5 component enlarges the band gap and increases the barrier height [6]. As a result, the resistance state changes to HRS.

Fig.7 shows the retention characteristic of TaOx ReRAM. For TaOx ReRAM, the resistance of HRS and LRS is almost constant after 3000 h at 150°C.

4. Conclusion
The origin of the resistive switching is attributed to the modulation of the barrier height between the anode and TaOx caused by the redox reaction. Excellent retention characteristic indicates that TaOx ReRAM is a promising device for next-generation high density nonvolatile memory.

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References
Figure 1 Potential energy curve of TaOₓ redox pair.

Figure 2 (a) Cross-section of the device with 4 electrode, (b) Resistance of regions (1) – (6) when the resistance of region (1) is switched.

Figure 3 (a) Top view and cross-section view of the large area test vehicle, (b) Ta 4d HX-PES spectra of TaOₓ large area test vehicle, insert is a cross section of the large area test vehicle, (c) Relative intensity ratio of TaO₂β/Ta₂O₅δ.

Figure 4 XPS spectra of TaOₓ near the anode and in the bulk.

Figure 5 Schottky plot of I-V curve of a TaOₓ ReRAM memory cell in pulse voltage sweep.

Figure 6 Modulation of the barrier height corresponding to redox reaction.

Figure 7 Data retention properties of TaOₓ ReRAM memory cells.