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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 (ΔG) 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 TaO_x 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 TaO_2/Ta_2O_5 showed the smallest reaction Gibbs energy. A schematic potential energy curve for TaO_x is shown in Fig.1. The redox reaction of TaO_x can be expressed as

$$2TaO_2+O^{2-} \longleftrightarrow Ta_2O_5+2e \qquad (1)$$

This indicates that both the high resistance state (HRS) and the low resistance state (LRS) of TaO_x are stable. In other words, TaO_x with redox pair of TaO_2/Ta_2O_5 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 × 20 μm². 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 TaO_x thin film. As shown in Fig.3(b) and Fig.3(c), the ratio of $TaO_{2-\beta}/Ta_2O_{5-\delta}$ increases with a sequence of initial, HRS and LRS, indicating that the $Ta_2O_{5-\delta}$ component is reduced to the $TaO_{2-\beta}$ 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 TaO_x thin film was controlled by annealing in oxygen ambient. X-ray Photoemission Spectroscopy (XPS) spectra show that the bulk material consists of only $TaO_{2-\beta}$, while $Ta_2O_{5-\delta}$ appears near the anode, where β and δ mean that the phases are close to TaO_2 and Ta_2O_5, respectively (Fig.4).

The optimized Pt/TaO_x/Pt memory cell with an area of 0.5 × 0.5 μm² shows excellent memory properties. The linear trend of $log(I)$-$V^{1/2}$ 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/TaO_x 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 TaO_x caused by the redox reaction (Fig.6). The interface layer between the anode and bulk TaO_x includes $Ta_2O_{5-\delta}$ and $TaO_{2-\beta}$. For a reset operation, by applying the positive voltage pulse on the anode electrode, O^{2-} ions migrate from the bulk TaO_x, which is assumed as an oxygen reservoir, and accumulate around the anode. Then the oxidization reaction of the $TaO_{2-\beta}$ and O^{2-} leads to the formation of the $Ta_2O_{5-\delta}$ according to the reaction formula (1). Increasing of the $Ta_2O_{5-\delta}$ 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 TaO_x ReRAM. For TaO_x 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 TaO_x caused by the redox reaction. Excellent retention characteristic indicates that TaO_x ReRAM is a promising device for next-generation high density nonvolatile memory.

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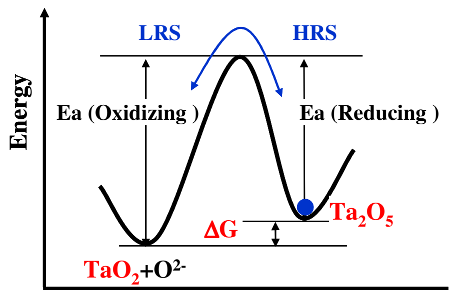


Figure 1 Potential energy curve of TaO_x redox pair

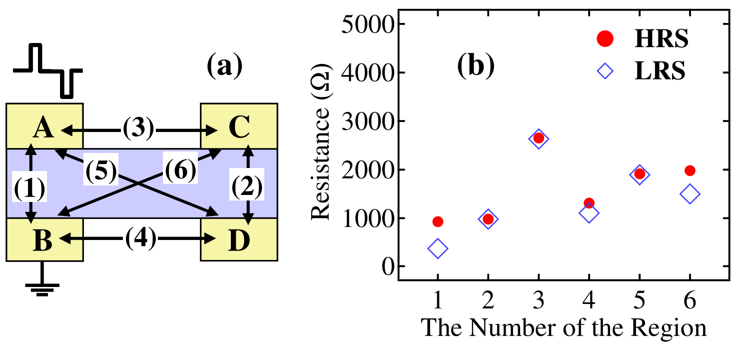
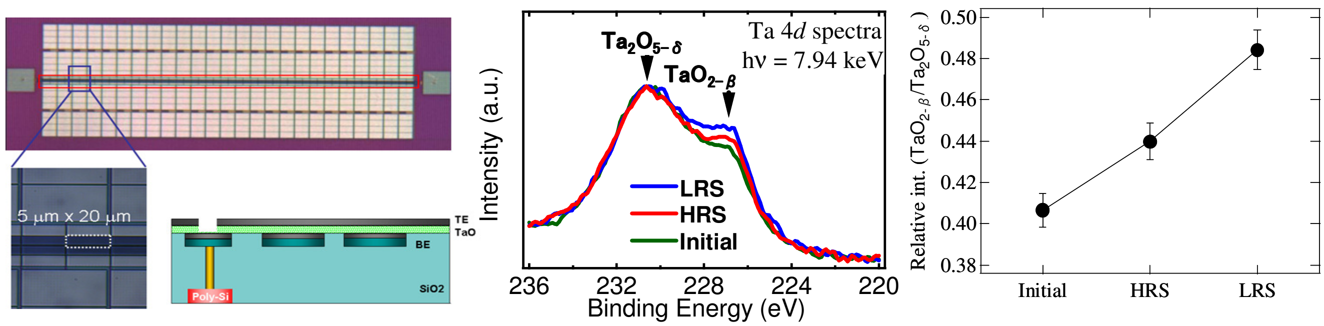


Figure 2 (a) Cross-section of the device with 4 electrode, (b) Resistance of regions (1) – (6) when the resistance of region (1) is switched.



(a) (b) (c)

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 $TaO_{2-\beta}/Ta_2O_{5-\delta}$

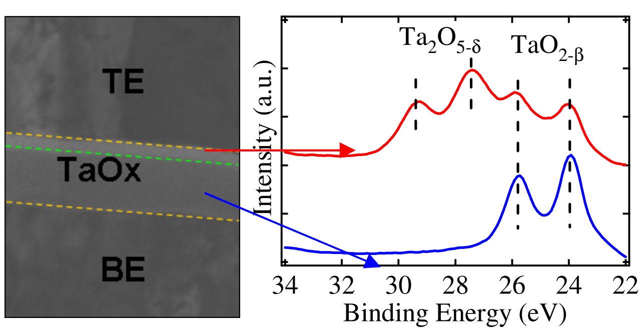


Figure 4 XPS spectra of TaO_x near the anode and in the bulk

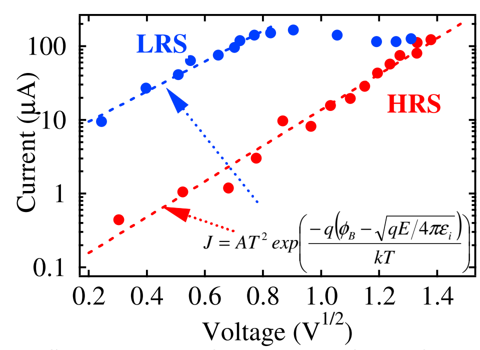


Figure 5 Schottky plot of *I-V* curve of a TaOx ReRAM memory cell in pulse voltage sweep.

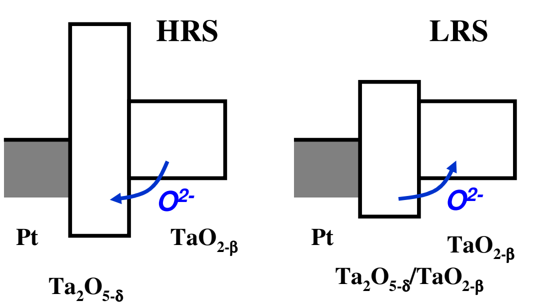


Figure 6 Modulation of the barrier height corresponding to redox reaction

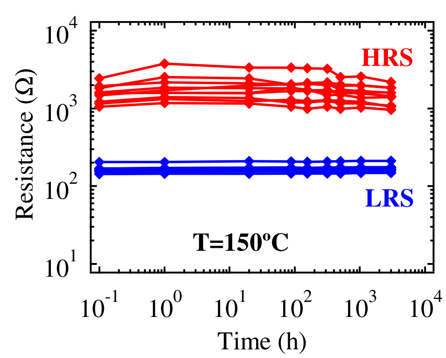


Figure7 Data retention properties of TaOx ReRAM memory cells