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Effects of Reactive Ti Creating Oxygen Vacancy Inside TiO_2 on Resistive Switching Characteristics in Resistive Random Access Memory Device

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Abstract

The effects of the reactive Ti layer on the resistive switching characteristics of TiO_2-based resistive random access memory (ReRAM) are investigated. The reactive Ti layer can act as a good oxygen gettering layer which makes the TiO_2 to have a higher concentration of oxygen vacancy, resulting in having better switching characteristics by varying the thickness of the Ti electrode.

1. Introduction

ReRAM has gained a lot of interests as one of the possible candidates of future non-volatile memory which can replace conventional flash memory. Recently, superior switching performance of HfO_2 using TiN/Ti electrode was reported [1], which shows good feasibility using conventional CMOS friendly metal electrode process. Also, TiO_2 was reported to have good switching characteristics [2]. However, it was done with Pt electrode, which may cause the process complexity due to the difficulty of Pt etch process.

In this paper, we use TiO_2 as a resistive switching material using the TiN/Ti electrode to investigate ReRAM switching characteristics and propose its mechanism dependent on the thickness of the Ti electrode.

2. Experimental

The TiN/Ti/TiO_2/TiN structure was fabricated using sub-50 nm process technology with 300 mm wafers. The TiO_2 was deposited by atomic layer deposition (ALD) or chemical vapor deposition (CVD) method on the bottom TiN electrode contact (~50 nm). After the TiO_2 deposition, the TiN/Ti top electrode was deposited by physical vapor deposition (PVD) method. Sequentially metal alloy anneal was conducted in a N_2 ambient at 400℃ for 10 min. The schematic process flow of the fabricated ReRAM structure is shown in Fig. 1. Electrical measurements and physical analysis using Electron energy loss spectroscopy (EELS) were conducted as well.

3. Result and Discussion

Figure 2 shows EELS analysis results for the non-patterned TiN/Ti/TiO_2/TiN/bare-Si structures (with/without the metal alloy anneal). As shown in Fig. 2(a), the compositional mapping shows that the Ti layer is partially nitrided during the TiN deposition which is done under a N_2 ambient. Fig. 2(c) shows the EELS spectrum of the TiO_2 layer without the alloy anneal, which shows typical TiO_2 O-K edge double peaks [3]. On the other hand, these TiO_2 peaks disappear after the alloy anneal, also oxygen is observed in the Ti region, as shown in Fig. 2(b). This means that TiO_2 becomes oxygen deficient TiO_{2-x}. The oxygen deoxidized from TiO_2 reacts with the partially nitrided Ti, causing a TiON layer formation. Accordingly, the inserted Ti layer on TiO_2 effectively produces oxygen vacancy inside TiO_2 during the alloy anneal. Fig. 2(d) summarizes the reactions at the TiO_2/Ti region during the alloy anneal. Therefore, we can expect good ReRAM switching properties of the TiO_{2-x} layer that is rich in oxygen vacancy.

Figure 3 shows DC I-V switching results for the Ti thickness of 0 Å, 50 Å, 100 Å on TiO_2 50 Å, respectively. The symbol and line is a first switching curve and lines are repeated switching curves. Fig. 3(a) shows switching results of the single TiO_2 50 Å (the Ti layer is skipped on the TiO_2 layer), where the initial state is high resistance state (HRS). Therefore, it requires SET process first under positive voltage bias to obtain low resistance state (LRS) and then RESET process to obtain HRS under negative voltage bias. The reset current can not be adjusted by compliance current (CC) and the switching variations are very large. On the contrary, Ti 50 Å and Ti 100 Å on TiO_2 50 Å show the different switching characteristics compared to the single TiO_2 50 Å sample, as shown in Fig. 3(b) and 3(c), respectively. Since the initial state of both samples are LRS, it requires RESET process first under negative voltage bias to obtain HRS and then SET process under positive voltage bias. The first reset currents show much higher values than those of CC. However, the following switching behaviors show that the reset currents are the same with CC and the switching variations are much smaller compared the single TiO_2 50 Å sample. Therefore, it is believed that the Ti layer on the TiO_2 acts a primary role to make a switching more stable. However, as the Ti thickness increases the on/off resistance ratio decreases due to the decrease of the initial resistance, as shown in Fig. 3(d). These results indicate that it is possible to obtain the best switching performance in terms of both the switching variation and the on/off resistance ratio.

Figure 4 shows the proposed switching mechanism based on these results. Since the single TiO_2 has little oxygen vacancy, the initial state is HRS like, as shown in Fig. 4(a). Switching occurs according to the applied voltage bias but the numbers of conductive filaments composed by oxygen vacancies inside TiO_2 are very small, leading to large switching variation, as shown in Fig. 3(a). On the other hand, the insert Ti layer on TiO_2 effectively produces oxygen vacancy inside TiO_2, which leads initial state to LRS, as shown in Fig. 4(b). The TiO_2 becomes TiO_{2-x}, creating a lot of oxygen vacancies inside during the alloy anneal as confirmed in Fig. 2. During the first RESET process (under negative voltage bias), oxygen is piled up at the bottom, creating insulative TiO_2 layer, which is confirmed by a linearity of Frenkel-Poole emission (F-P) fitting, as shown in Fig. 5. This means the first RESET occurs by the interface reaction of oxygen ion at the bottom of the TiO_2. During SET process under the following positive voltage bias, conductive filaments are created from the bottom of TiO_2 [4]. However, the insulative TiO_2 layer created at the bottom during the first RESET process makes it difficult to create conductive filaments that have to grow from the bottom, requiring high voltage to make first SET. After the first SET process, the following switchings are made by the filament connection/disconnection. Therefore, the following RESET voltage is smaller than that of the first RESET because the switching is made by local filament conduction. Based on this model, the resistance of HRS should be dependent on the concentration of oxygen vacancy in TiO_2 at disconnected region of the filaments. With increased thickness of Ti, the concentration of oxygen vacancy should be increased, leading to the decreased on/off resistance ratio due to the decreased resistance of HRS, as shown in Fig. 4(c). Accordingly, the on/off resistance ratio can be adjusted with varying the thickness of Ti.

Figure 6 and Fig. 7 show the reliability characteristics obtained by adjusting the thickness of Ti and TiO_2. The switching endurance characteristics are measured in DC sweep mode and achieved more than 2×10^4 cycles, as shown in Fig. 6(a) and 6(b). During a retention test measured at the temperature of 200°C and 225°C, the current levels are stable for more than 4000 sec., as shown in Fig. 7.

4. Conclusion

The peculiar characteristics and the model of ReRAM switching of the Ti/TiO_2 resistive material depending on the thickness of Ti have been studied. The Ti layer deposited on the TiO_2 performs the role of providing oxygen vacancy inside the TiO_2 during the annealing. The amount of the created oxygen vacancy can be controlled by varying the thickness of Ti and TiO_2, which allows the control of resistance switching characteristics. Using the fabricated TiN/Ti/TiO_2/TiN nano-structure with the Ti thickness of 50 Å, we obtain the satisfactory DC endurance as well as retention properties.

References

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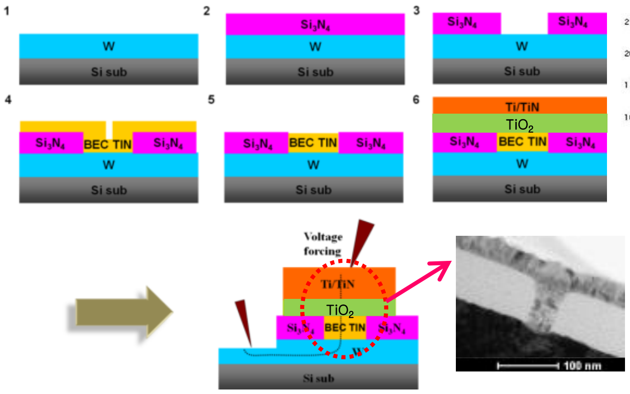

Fig.1. Schematic process flow of fabricated ReRAM structure. The Bottom electrode contact (BEC) size is 50nm.

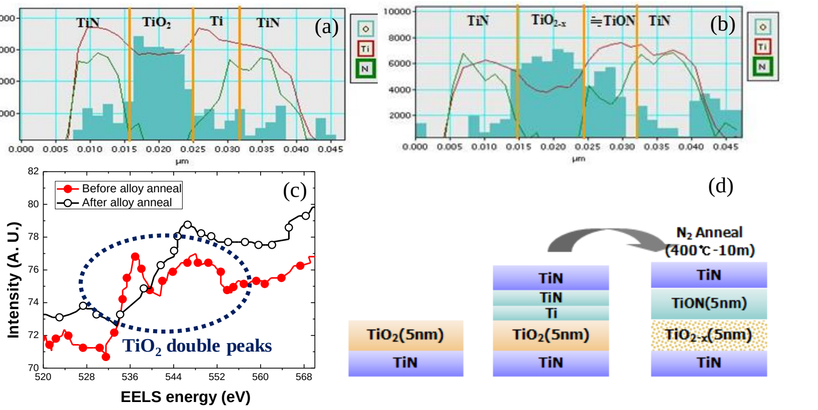

Fig.2. EELS analysis results for the non-patterned TiN/Ti/TiO_2/TiN/bare-Si structures compositional mapping data (a) without the alloy anneal , (b) with the alloy anneal, (c) EELS spectrum inside TiO_2 region with/without the alloy anneal, and (d) with the summary of its reactions at the TiO_2/Ti region during the alloy anneal.

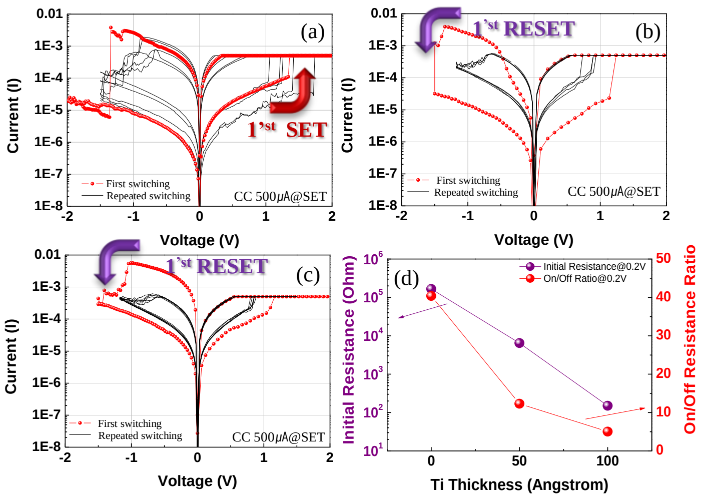

Fig.3. DC I-V switching results for the various Ti on the TiO_2 50 Å (a) single TiO_2 50 Å (Ti is skip on TiO_2), (b) Ti 50 Å on the TiO_2 50 Å, (c) Ti 100 Å on the TiO_2 50 Å, and (d) initial resistances and on/off resistance ratio for various Ti thickness.

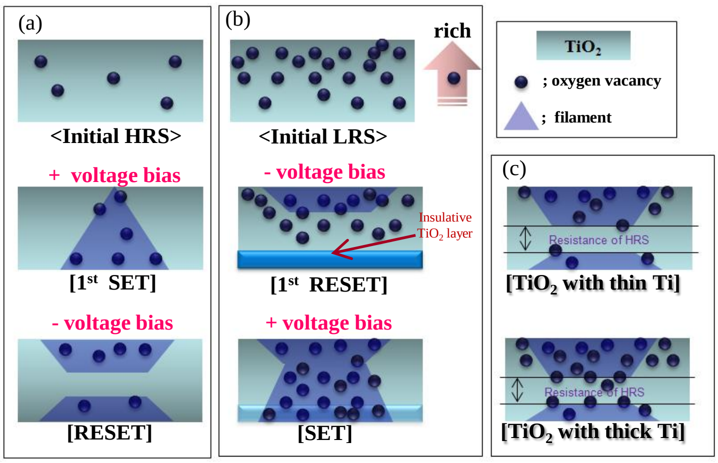

Fig.4. Proposed switching mechanism (the shape of filament is exaggerated for the clear explanation). (a) single TiO_2 50 Å (Ti is skiped on TiO_2), (b) Ti on TiO_2, and (c) the effect of Ti thickness on on/off resistance ratio.

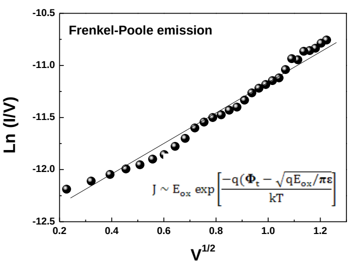

Fig.5. F-P fitting for the first RESET state in Ti 50 Å/TiO_2 50 Å.

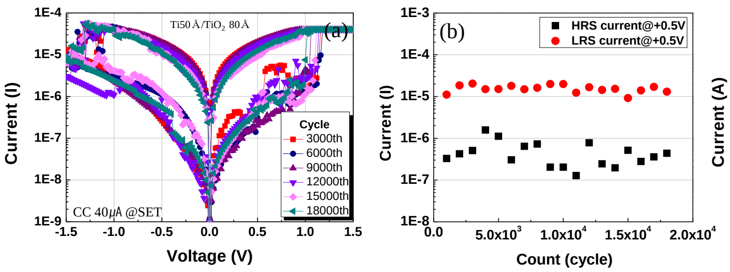

Fig.6. The endurance characteristics measured in DC sweep mode. (a) Cumulative switching curves at CC 40uA, (b) The HRS and LRS currents are measured at 0.5V.

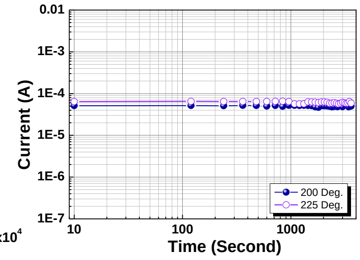

Fig.7. Retention characteristics measured at the temperature of 200˚C and 225˚C.