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Low Power and Highly Reliable Gadolinium Oxide Resistive Switching Memory with Remote NH_3 Plasma Treatment

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1. Introduction

Owing to the scaling limitation of flash memory, many problems as if low program/erase speed and poor data retention. Resistive random access memory (RRAM) is one of the alternative approaches being investigated for next generation [1]. Among the various candidates, the simple metal-insulator-metal structure with a transition metal oxide (TMO) material, such as TiO_2 and ZrO_2 , has been shown to exhibit excellent bistable resistive switching behavior[2,3]. Recently, gadolinium oxide had been proposed to be applied in RRAM [4]. The formation and rupture of the conducting filamentary paths of oxygen vacancies is responsible for the resistive switching of the gadolinium oxide RRAM. In this work, the characteristics of gadolinium oxide resistive switching memory with remote NH_3 plasma treatment were investigated. With optimized treatment time, the HRS/LRS ratio is increased. Furthermore, with remote NH_3 plasma treatment, the incorporation of nitrogen ions at Pt/GdO_x surface can induce more oxygen vacancies and suppress the movement of oxygen ions. Thus, the endurance/ retention properties became more stable.

2. Experiment

Gadolinium oxide resistive switching memory structure was fabricated on 4-inch SiO_2/ Si wafers. Next, a 100nm tungsten bottom electrode was deposited by dc sputtering method. Then, a 20nm amorphous gadolinium oxide was deposited by sputtering with Gd target (99.9% pure) in oxygen and argon mixture ambient (O_2:Ar=12:6). Subsequently, the key process of remote NH_3 plasma at 30W was then treated on GdO_x for 20 and 30min by atomic layer chemical vapor deposition (ALCVD) system. After that, a 50 nm platinum top electrode was deposited by E-beam evaporator, and the 20μm in diameter was defined by lift-off process. Finally, the post metallization annealing (PMA) at 300°C for 10min was conducted. The detailed process flow was shown in Fig. 1. The electrical properties of the samples were measured by using the Agilent 4156C analyzer. The X-ray Photoelectron Spectroscopy (XPS) and Ultraviolet Photoelectron Spectroscopy (UPS) were applied to measure film composition, Fermi level position of GdO_x films for explaining this model.

3. Results and Discussion

Fig. 2(a) and (b) show the O 1s XPS spectra of GdO_x films without and with remote NH_3 plasma treatment, respectively. The non-lattice oxygen peak decreases due to the increasing amount of oxygen interstitial and vacancy by remote NH_3 plasma treatment, resulting in the generation of more portative oxygen vacancies [5]. Fig. 3(a) shows the bipolar resistance switching behavior of all samples. The set and reset processes are operated at negative and positive voltages, respectively. In our previous work of NH_3 plasma treatment, even though the set/ reset voltage was decreased, the reset process was insignificant, resulting in the reduction of HRS/LRS ratio [6]. The switching property of the sample with remote NH_3 plasma treatment is more stable during ten switching cycles, as shown in Fig. 3(b). Fig. 5(a) and (b) demonstrates the set/reset voltage, high/low resistance state (HRS/LRS) and ratio characteristics, respectively. Because the defects are slightly generated by remote plasma damage, the device with 20 min treatment time can be operated stably for only 1000 cycles, as shown in Fig. 4. Fig. 6 shows the charge retention properties of GdO_x RRAM with remote NH_3 plasma treatment. Nitrogen incorporation will prevent the Pt out-diffusion and improve the retention. The UPS result is shown in Fig. 7. It is obtained by using a UV He lamp (21.2 eV) in an ultrahigh vacuum chamber. A broad spectral feature representative of the Fermi level position (E_F) above valence band of GdO_x was observed at lower binding energies. It's about 4.07 eV. This indicates that GdO_x is an n-type oxide, which is identical with ref.[6] (the band gap of GdO_x is 5.39 eV in [6]). The I–V curve in the HRS can be fitted well by a Schottky-like emission relationship, as shown in Fig. 8:

$$J = A^* T^2 \exp\left\{\left(-\Phi_B / kT\right)\left(q^3 V / 4\pi\varepsilon_0\varepsilon_{ox} t_{ox}\right)^{1/2}\right\} \qquad (1)$$

The barrier height between Pt top electrode and the conduction band of GdO_x with remote NH_3 plasma treatment is lower than that without treatment. Due to the decrease of the barrier, the set and reset processes become much easier. However, the Schottky current was also generated easily, leading to the lower HRS. Fig. 9 shows schematic band diagrams of mechanism of Pt/GdO_x RRAM with remote NH_3 plasma treatment.

4. Conclusion

In this work, the Pt/GdOx/W RRAM properties such as set/rest voltages and retention/endurance characteristics were improved by using low damage remote NH_3 plasma treatment. The enhancement was attributed to the nitrogen incorporation and revealed by the material analysis.

Acknowledgements

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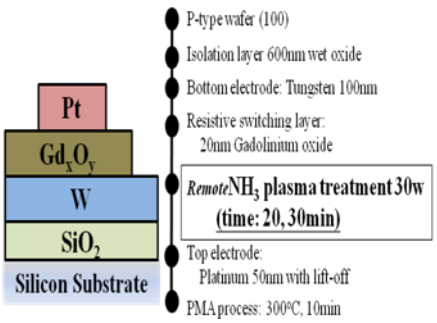

Fig. 1 The fabrication procedure of Pt/GdO_x/W RRAM with and w/o remote NH_3 plasma treatment.

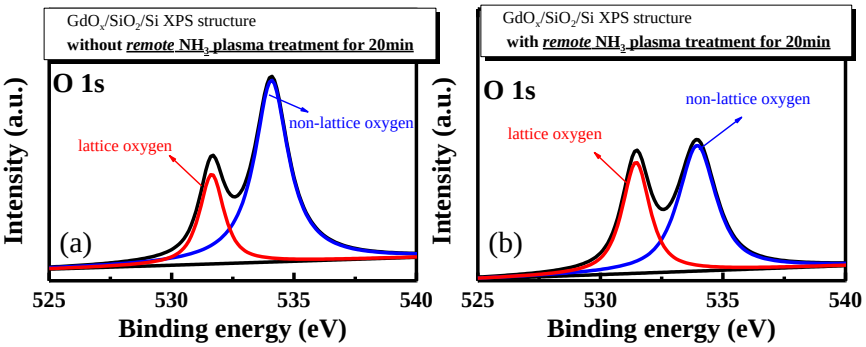

Fig. 2 O 1s XPS spectra of the GdO_x films (a) w/o and (b) with remote NH_3 plasma treatment. The non-lattice oxygen peak was decreased by remote NH_3 plasma treatment, meaning that the oxygen vacancies were reduced.

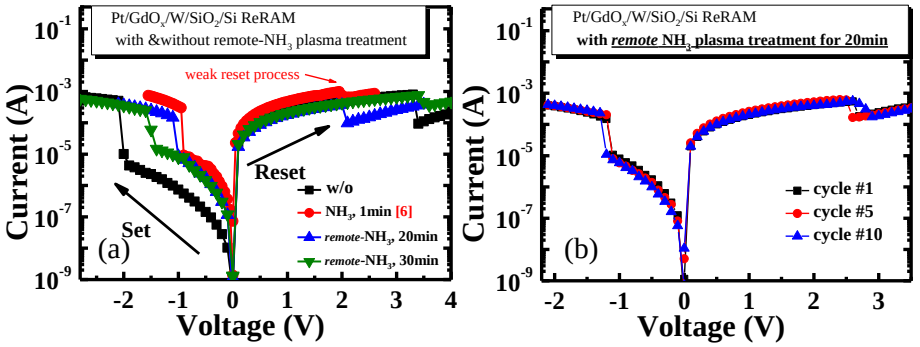

Fig. 3 (a) Bipolar current-voltage characteristics of GdO_x RRAM without and with remote NH_3 plasma treatment. (b) Current-voltage characteristics of GdO_x RRAM with remote NH_3 plasma treatment after 1, 5, and 10 cycling.

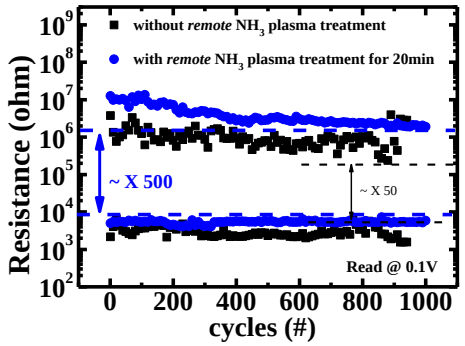

Fig. 4 The endurance properties of GdO_x RRAM with remote NH_3 plasma treatment. The endurance become stable

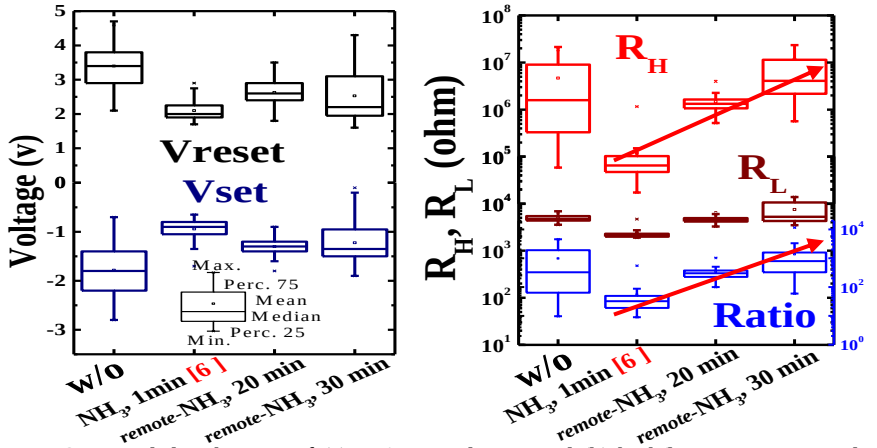

Fig. 5 Statistical distributions of (a) set/reset voltages, and (b) high/low resistances and resistance ratio of GdO_x RRAM with and w/o remote NH_3 plasma treatment. The samples with remote NH_3 plasma treatment demonstrate high HRS/LRS ratio.

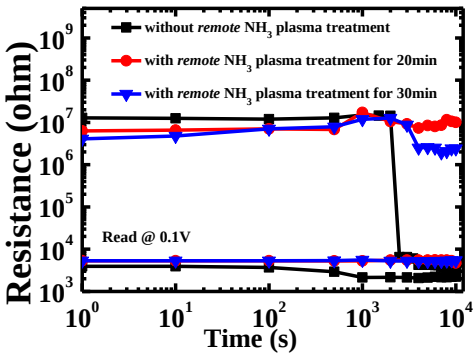

Fig. 6 Charge retention properties of GdO_x RRAM with and w/o remote NH_3 plasma treatment. Nitrogen incorporation will prevent the oxygen out-diffusion through Pt.

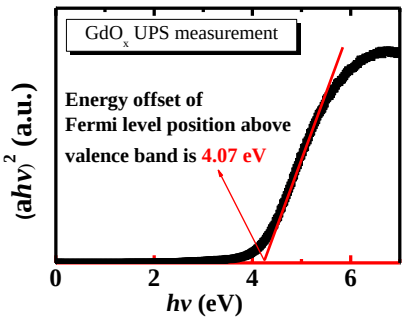

Fig. 7 Energy offset of Fermi level above valence band edge of GdO_x film obtained from UPS.

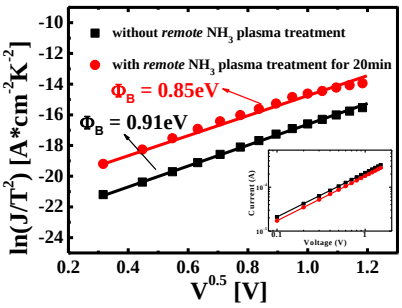

Fig. 8 Schottky emission fitting of HRS for the samples with and w/o remote NH_3 plasma treatment. The inset figure shows the LRS fitted by ohmic.

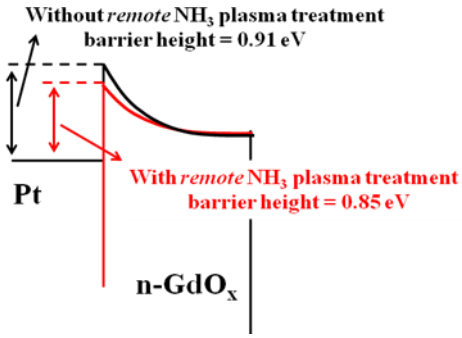

Fig. 9 Schematic diagram of the mechanisms of Pt/GdO_x RRAM with and w/o remote NH_3 plasma treatment.