Improved Resistive-switching Performance of HfO₂-based RRAM devices by Reduction Effect of Hydrogen Annealing: Defect Engineering

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1. Introduction

Resistive random access memory (RRAM) has attracted as a promising candidate for next generation of non-volatile memory device due to their simple structure, fast switching speed, low power consumption, and excellent scalability [1-2]. However, switching non uniformity and unclear switching mechanisms need to be solved [3-5]. In this study, we propose a new and effective methodology for improving the resistive-switching performance by subjecting HfO_2 films to high-pressure hydrogen annealing (HPHA) under ambient conditions. The reduction effect caused by hydrogen atom impurities on the HPHA-treated HfO_2 films increases generated many Vo in the initial state, and uniform conducting filament (CF) can be formed by the precise control of the oxygen vacancy (Vo).

2. Experimental

A 100-nm-thick of PECVD-grown SiO₂ dielectric layer was deposited on top of 8" Pt/SiO₂/Si stack wafers. After conventional lithography and etching process, a 250-nm via-hole structure was defined with Pt bottom electrode (BE). A 5-nm-thick HfO₂ layer was deposited using ALD with TEMAH and H₂O precursors. And then, HfO₂ layer slated for high-pressure annealing was treated at 200 °C under ambient H₂ at 10 atm for 30 min (HPHA sample) [6]. The control sample was also prepared without HPHA treatment for the comparison. Finally, 50-nm-thick TiN top electrode (TE) was deposited by the rf magnetron sputtering method.

3. Results & Discussion

To investigate the effect of hydrogen on HfO₂ based RRAM devices, we analyzed the electrical and physical characteristics of TiN/HfO₂/Pt stack with HPHA treatment. Figure 1(a) exhibits the representative initial current-voltage (I-V) curve set of randomly selected 30 devices of the TiN/HfO₂/Pt stack. The voltage was applied to the TiN TE, while Pt BE was grounded. To initiate the resistive switching operation in HfO₂, the forming process, which initially make the local CFs induced by Vo was necessary. It is clearly found that the current value of red line, which represents the forming current of HPHA samples, is higher than that of blue line, which depicts control samples. In other words, the initial resistance values are decreased from $78.6G\Omega$ to $9.2M\Omega$ after HPHA treatment. Moreover, the average of forming voltage of 30 devices was also decreased from 2.68 V to 1.18 V, which means forming-free operation (Fig. 1(b)). This phenomenon is attributed to the reduction effect on HfO₂ film by diffusion of hydrogen atom impurities at a high pressure ambient. As the hydrogen atoms diffuse into the HfO₂ film, lots of Vo in the HfO₂ were generated by reduction effect, which results in decrease of its resistivity. Thus, HPHA is effective way to generate Vo in binary oxide film at a relatively low temperature process. To examine the effect of the generation of Vo on the switching uniformity, the various switching parameters between control and HPHA samples were compared. Figure 2 represents the typical I-V characteristics of TiN/HfO₂/Pt device. The compliance current was set to the $50 \,\mu\text{A}$ in order to prevent permanent breakdown during the set

operation. While the switching uniformity of control samples shows very poor, the HPHA samples show better uniformity. The more detail switching parameters are summarized as shown in Fig. 3. The results show tight distribution of switching parameters, such as HRS, LRS current, and SET voltage in 50 devices with HPHA. Moreover, the reduction in the maximum reset current below was 50 μ A also obtained.

To physically investigate the reduction effect by hydrogen atom, the various analyses were performed. Figure 4 shows C-AFM images of HfO₂ layer using Pt-coated tip. In HPHA samples, lots of current peaks were observed due to generation of Vo clusters by reduction effect, while no current peak observed in control samples. To clarify the effect of hydrogen atom, we measured TOF-SIMS of TiN/HfO2/Pt stack as shown in Fig. 5. Clearly, H ion intensity of HPHA samples is much higher than that of control sample from the TOF-SIMS measurement, which indicates that the hydrogen atom impurity was successfully formed in the HfO₂ bulk layer by HPHA process. Moreover, figure 6 exhibits FT-IR measurement, which indicates that OH bonding was formed by hydrogen atom diffusion. The combination of the hydrogen and oxygen ions also results in the formation of hydroxyl (OH⁻) mobile ion in HfO₂ bulk layer. The excellent retention characteristic was achieved as shown in Fig. 7. Both LRS and HRS states are well maintained at high temperature (~200°C) more than for 10⁴s. The generation of OH⁻ mobile ion with hydrogen atom, and reduction effect improve resistive switching performance as shown in Fig 8. We set up the real-time oscilloscope measurement to monitor switching delay time by applying pulse voltage during SET operation. Fig. 8 (a) shows mean delay time during SET operation, which indicates that delay time was significantly decreased in HPHA samples. Moreover, Fig. 8 (b) shows the fast pulse switching operation by applied pulse voltage (4V, 1µs). The improvement of switching speed could be explained that the effective barrier for SET/RESET switching by an oxygen ion movement is lowered by lots of generation of Vo and OH⁻ ion due to HPHA treatment as illustrated in Fig. 8 (c). Finally, the proposed reduction effect and switching mechanism in HfO₂-based RRAM devices is schematically illustrated in Fig. 9. Therefore, hydrogen atom impurity not only improves device performances such as uniformity and switching speed of HfO₂ based RRAM devices, but also does not significantly affect the retention characteristics. 4. Summary

In this paper, defect engineering like hydrogen atom impurity was performed to improve device performance such as, uniformity and switching speed in HfO₂-based RRAM devices. By HPHA treatment, the forming free operation and excellent uniformity characteristics were obtained by reducing effect of hydrogen atom impurity. Furthermore, fast switching operation was also achieved due to generation of mobile ions in bulk HfO₂ layer. Based on the results, hydrogen treatment could be an effective way to improve device performance for the metal oxide based RRAM device applications.

Acknowledgments

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Fig. 1. Forming *I-V* curves of 30 randomly selected devices with a $TiN/HfO_2/Pt$ stack. The blue line indicates the forming current of the control samples, whereas the red line indicates that of HPHF samples. (b) Distribution of the initial resistance of HfO_2 and the average of the forming voltage during the forming process.

Fig. 2. Typical *I-V* characteristics of the $TiN/HfO_2/Pt$ stack after HPHA treatment. The compliance current was set to 50μ A.



Fig. 3. Comparison between resistive-switching parameters of the control and HPHA samples, which shows the switching uniformity of 50 randomly selected devices. (a) Current in LRS and HRS (b) Maximum RESET current and SET voltage.



Fig. 5. (a) TOF-SIMS depth profile of HPHA-treated $TiN/HfO_2/Pt$ stack. (b) Comparison between H+ ion intensity of the control and HPHA samples.



Fig. 8. Real-time oscilloscope measurement during SET operation. The effective barrier for oxygen ion movement is lowered by the generation of many Vo and OH ions owing to HPHA treatment.

Fig. 4. C-AFM scan image of HfO_2 film read at 0.5 V prior to the forming process. No current peak (~pA) was observed in the control sample, whereas many current peaks (~1nA) were observed due to Vo clusters after HPHA treatment.



Fig. 6. FT-IR analysis indicating existence of OH bonds that are formed by the combination of oxygen and hydrogen ions after HPHA treatment.

Fig. 7. Retention characteristics of HPHA samples at various temperature. Both LRS and HRS are well maintained at high temperature ($\sim 200^{\circ}$ C) for more than 10^{4} s.



Fig. 9. Schematic illustration of reduction effect of hydrogen atom impurities on switching uniformity (a) Diffusion process of hydrogen atom impurities in HfO_2 bulk layer (b) Hydrogen atoms create Vo and OH⁻ ions because of the reduction effect. (c) After the deposition of the TE, a dominant CF is generated along a preferential path by the pre-existing Vo (SET operation). (d) The rupture of CF induces HRS (RESET operation).