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Enhancement of Resistive Switching in Cu/HfO_2/Pt Structures by Providing Water

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Abstract

Atmosphere dependence of resistive switching parameters of conducting-bridge random access memory (CB-RAM) was studied by taking advantage of Cu-probe/HfO_2/Pt structures which ensure high permeability to both gasses and liquids. Only H_2O among the constituent of the atmosphere (H_2O, N_2, O_2, and vacuum) strongly affects resistive switching parameters and lowers a reset current and a set and forming voltages drastically. This lowering effect is weakened with decreasing temperature from room temperature to -40 °C, suggesting that H_2O as a liquid water is closely related to the mechanism of a set and forming processes and enhances the migration of Cu ions.

1. Introduction

A high CMOS compatibility and the improvement of data retention was achieved in conducting-bridge memory (CB-RAM) in which the selenide [1] or sulifide [2] layer was replaced with a metal oxide (MO) layer. However, the mechanism and the path for migration of atoms constituting the active electrode in MOs which are not necessarily categorized as solid electrolytes have not yet been clarified. In addition, serious issue that a current to cause a reset process [3], I_{reset}, increases in MO-based CB-RAM was raised, where a reset is resistive switching from low to high resistance states. Mechanism elucidation is crucial for controlling and optimizing memory characteristics. Under such circumstance, it was reported that moisture that was absorbed in the MO layer affects the resistive switching property [4].

In this paper, the effect of atmosphere (H_2O, N_2, O_2, and vacuum) on the resistive switching property of Cu-probe/HfO_2/Pt structures was investigated. As a result, it was shown that only H_2O impacted on resistive switching among the constituents of the atmosphere and reduced I_{reset} drastically.

2. Experimental

HfO_2 layer with thickness of 25 nm was deposited on a Pt (100 nm)/Ti (20 nm)/SiO_2 (100 nm)/Si (650 µm) substructure in the mixed gas of Ar and O_2 (Ar : O_2 = 3.8 : 1.5 Pa) by using RF reactive sputtering method. Total gas pressure, RF power and substrate temperature were maintained at 5.3 Pa, 100 W and 300 °C, respectively. By contacting the surface of the HfO_2 film with a Cu-probe, a Cu-probe/HfO_2/Pt structure was constituted. The voltage was applied to the Cu-probe, whereas the Pt-electrode was grounded. Current compliance value, I_{comp}, was set to 100 µA for all the forming and set processes. Atmosphere dependences of *I-V* characteristics were measured in a vacuum chamber. The effects of N_2 and O_2 on *I-V* characteristics were measured after vacuuming the chamber to 10^{-5} Pa and replacing the air with N_2 or O_2 gasses. The effect of H_2O on *I-V* characteristics was measured by dropping a small amount of ultrapure water on the HfO_2 surface using a dropper and contacting the HfO_2 surface with the Cu-probe through the drop of water.

3. Results and Discussion

Fig. 1(a) shows *I-V* characteristics of Cu-probe/HfO_2/Pt structure measured in air, by contacting the HfO_2 surface with a Cu-probe at room temperature (RT). Set and reset occurred by applying positive and negative voltages to the Cu-electrode, respectively, after going through a forming process. Fig. 1(b) shows *I-V* characteristics of the same structure measured in H_2O. Figs. 2(a), 2(b), and 2(c) show dependences of cumulative probabilities on the kind of atmosphere gas for forming (V_f), reset (V_{reset}), and set (V_{set}) voltages, respectively. Average V_f values in H_2O and in air were 6.95 V and 4.28 V, respectively, which were lower than those measured in other atmospheres. The similar trend was observed in V_{set}, suggesting that the presence of H_2O is related to the lowering of both V_f and V_{set}. On the other hand, V_{reset} was independent of atmosphere.

Fig. 3(a) shows the $1/R_{LRS}$-dependence of I_{reset} on atmosphere. All the I_{reset} data obey the universal relation of $I_{reset} \propto 1/R_{LRS}$, which was reported to be satisfied in air [5]. This suggests that reset occurs basing on the unified mechanism, regardless of the presence of H_2O. In addition, I_{reset} in H_2O is smaller than I_{reset} in other atmospheres, although all the I_{reset} data is larger than I_{comp} of 100 µA. Fig. 3(b) shows the V_{set}-dependence of I_{reset} in several atmospheres. I_{reset} in atmospheres other than H_2O obeys the relationship of $I_{reset} \propto 1/R_{LRS}$, whereas I_{reset} in H_2O deviates to much lower values from the relationship. This result shows that the relationship of $I_{reset} \propto V_{set}$, which is true in air, is drastically modified by the presence of H_2O, and I_{reset} can be reduced without decreasing parasitic capacitance between the memory device and a current limiter [5].

Fig. 4 shows *I-V* characteristics measured in H_2O at -40 °C. *I-V* characteristics measured in H_2O and in air at RT are also shown in Fig. 4. Decreases in both R_{HRS} and V_{set} by supplying water at RT were restored at temperature below 0 °C. This is due to the freezing of water that was absorbed into gaps between columnar HfO_2 grains (inset of Fig. 4) by capillarity.

Figs. 5(a) and 5(b) show cumulative probabilities of V_f and V_{set} in H_2O at several temperatures, respectively. V_f and V_{set} in vacuum were also shown for comparison. Both V_f- and V_{set}-distributions in H_2O increase toward V_f- and V_{set}-distributions in vacuum with decreasing temperature, respectively, although they did not agree with each other even at -40 °C. This is consistent with the report that freezing point of water that is confined in a pore decreases with decreasing pore diameter [6].

4. Conclusion

H_2O as a liquid water enhanced a set and forming processes in $Cu/HfO_2/Pt$ structures, which appears to lead the reduction of I_{reset}. This suggests that the migration of Cu ions is mediated by H_2O. Therefore, elucidation of the role of H_2O in resistive switching is a key for further improvement of the performance.

References

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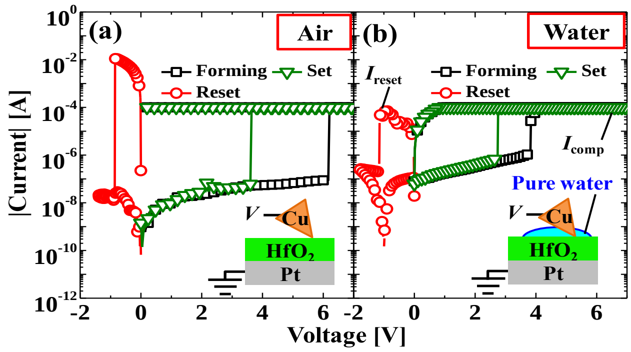

Fig. 1 *I-V* characteristics of Cu-probe/HfO_2/Pt structures (a) in air and (b) in H_2O.

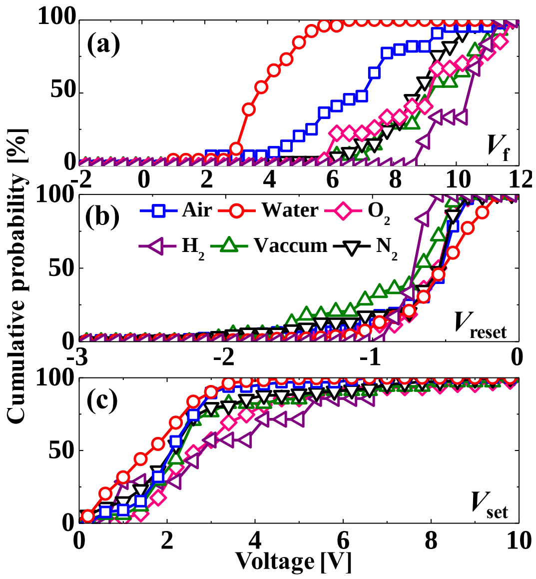

Fig. 2 Cumulative probabilities of (a) V_f, (b) V_{reset}, and (c) V_{set}.

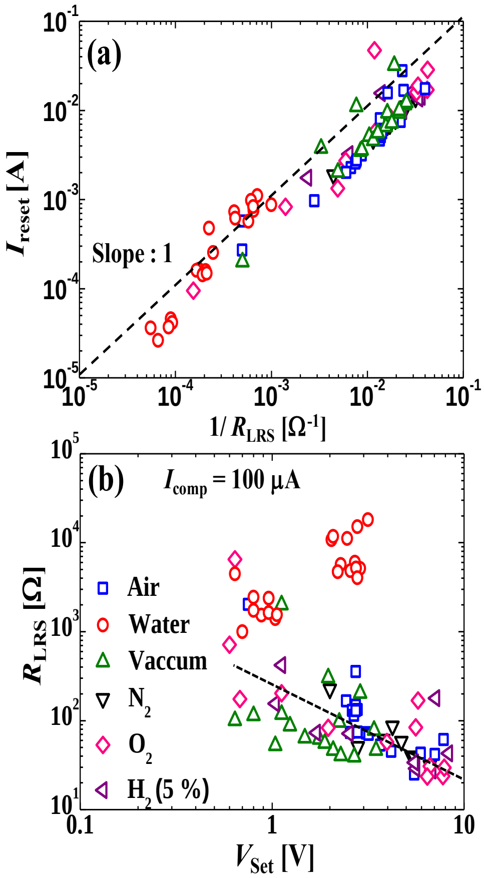

Fig. 3 (a) 1/ R_{LRS}-dependence of I_{reset}. (b) V_{set}-dependence of I_{reset}.

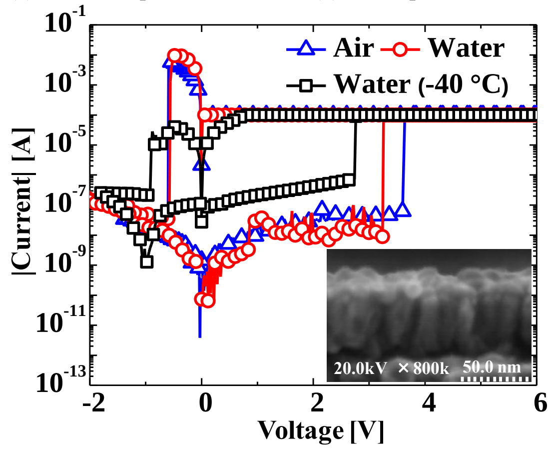

Fig. 4 *I-V* characteristics measured in H_2O at -40 °C. *I-V* characteristics measured in H_2O and in air at RT are also shown. Inset: cross-sectional SEM image of the HfO_2 layer.

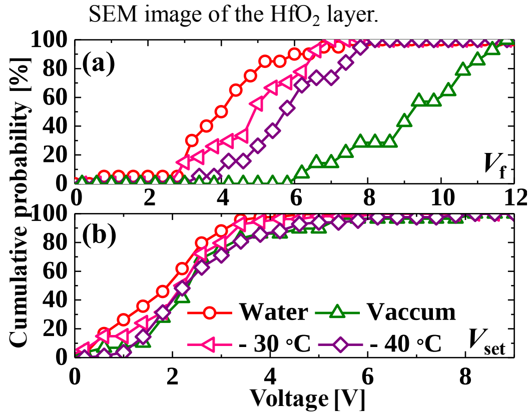

Fig. 5 Cumulative probabilities of (a) V_f and (b) V_{set} in H_2O at several temperatures. Cumulative probabilities in vacuum are also shown for comparison.