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$_2$O among the constituent of the atmosphere (H$_2$O, 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$_2$O 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], $I_{\text{reset}}$, 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$_2$O, 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$_2$O impacted on resistive switching among the constituents of the atmosphere and reduced $I_{\text{reset}}$ 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, $I_{\text{comp}}$, 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 evacuating the chamber to 10$^{-3}$ Pa and replacing the air with N$_2$ or O$_2$ gasses. The effect of H$_2$O 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$_2$O. Figs. 2(a), 2(b), and 2(c) show dependences of cumulative probabilities on the kind of atmosphere gas for forming ($V_f$), reset ($V_{\text{reset}}$), and set ($V_{\text{set}}$) voltages, respectively. Average $V_1$ values in H$_2$O 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 $V_{\text{reset}}$, suggesting that the presence of H$_2$O is related to the lowering of both $V_1$ and $V_{\text{reset}}$. On the other hand, $V_{\text{set}}$ was independent of atmosphere.

Fig. 3(a) shows the 1/$R_{\text{LRS}}$-dependence of $I_{\text{reset}}$ on atmosphere. All the $I_{\text{reset}}$ data obey the universal relation of $I_{\text{reset}} \propto 1/R_{\text{LRS}}$, 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$_2$O. In addition, $I_{\text{reset}}$ in H$_2$O is smaller than $I_{\text{reset}}$ in other atmospheres, although all the $I_{\text{reset}}$ data is larger than $I_{\text{comp}}$ of 100 μA. Fig. 3(b) shows the $V_{\text{reset}}$-dependence of $I_{\text{reset}}$ in several atmospheres. $I_{\text{reset}}$ in atmospheres other than H$_2$O obeys the relationship of $I_{\text{reset}} \propto 1/R_{\text{LRS}}$, whereas $I_{\text{reset}}$ in H$_2$O deviates to much lower values from the relationship. This result shows that the relationship of $I_{\text{reset}} \propto V_{\text{reset}}$, which is true in air, is drastically modified by the presence of H$_2$O, and $I_{\text{reset}}$ 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$_2$O at -40°C. $I$-$V$ characteristics measured in H$_2$O and in air at RT are also shown in Fig. 4. Decreases in both $R_{\text{HRS}}$ and $V_{\text{set}}$ 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 $V_{\text{set}}$ in H$_2$O at several temperatures, respectively. $V_f$ and $V_{\text{set}}$ in vacuum were also shown for comparison. Both $V_f$- and $V_{\text{set}}$-distributions in H$_2$O increase toward $V_f$- and $V_{\text{set}}$-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$_2$O as a liquid water enhanced a set and forming processes in Cu/HfO$_2$/Pt structures, which appears to lead the reduction of $I_{\text{reset}}$. This suggests that the migration of Cu ions is mediated by H$_2$O. Therefore, elucidation of the role of H$_2$O in resistive switching is a key for further improvement of the performance.

References

![Fig. 1 I-V characteristics of Cu-probe/HfO$_2$/Pt structures (a) in air and (b) in H$_2$O.](image1)

![Fig. 2 Cumulative probabilities of (a) $V_f$, (b) $V_{\text{reset}}$, and (c) $V_{\text{set}}$.](image2)

![Fig. 3 (a) $1/R_{\text{LRS}}$-dependence of $I_{\text{reset}}$. (b) $V_{\text{set}}$-dependence of $I_{\text{reset}}$.](image3)

![Fig. 4 I-V characteristics measured in H$_2$O at -40 °C. I-V characteristics measured in H$_2$O and in air at RT are also shown. Inset: cross-sectional SEM image of the HfO$_2$ layer.](image4)

![Fig. 5 Cumulative probabilities of (a) $V_f$ and (b) $V_{\text{set}}$ in H$_2$O at several temperatures. Cumulative probabilities in vacuum are also shown for comparison.](image5)