Switching Mode and Mechanism in Binary Oxide Resistive Random Access Memory Using Ni Electrode

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Resistive-switching (RS) modes in different CMOS-compatible binary oxides have been shown to be governed by the interplay with the Ni top electrode. Unipolar RS and metallic low-resistance state in polycrystalline HfO₂ and ZrO₂ are distinct from the preferential bipolar RS and semiconductive low-resistance state in amorphous Al₂O₃ and SiO₂. Backside secondary ion mass spectrometry (SIMS) shows the formation of Ni filaments in HfO₂, in contrast to the formation of oxygen-vacancy filaments in Al₂O₃. The differences have been explained by strong dependence of Ni migration on the oxide crystallinity. Additionally, the RS mode can be further tailored using bilayer structures. The oxide layer next to the Si bottom electrode and its tendency of forming Ni filaments play significant roles in unipolar RS in the bilayer structures, in support of the conical-shape Ni filament model where the connecting and rupture of filaments for unipolar RS occur at the smallest diameter near the bottom electrodes.

1. Introduction

Resistive random access memory (RRAM) employs reversible resistive switching (RS) between low resistance state (LRS) and high resistance state (HRS) in simple metal-insulator-metal (MIM) structures for nonvolatile information storage.¹,² In redox-based RRAM, RS has been reported to occur at local conductive filaments comprising either oxygen vacancies or metal ions in insulators. By applying appropriate SET/RESET voltage ($V_{\text{SET}}/V_{\text{RESET}}$) between top and bottom electrodes, the connecting and rupture of conducting filaments are triggered by three major physical mechanisms and results in different bipolar RS (BRS) and unipolar RS (URS) modes, namely electrochemical metallization of metal filaments for BRS, valance change effect of oxygen-vacancy filaments for BRS, and thermochemical effect for URS when Joule heating is predominant at RESET.²

Among a wide range of materials showing RS phenomena, such as perovskite oxides, ferromagnets, chalcogenides, and binary metal oxides,³–⁶ the binary metal oxides such as HfO₂ have been the most interesting because of their compatibility with advanced CMOS technology.⁷,⁸ Furthermore, the RS modes in RRAM had been shown to depend strongly on the metal electrodes using an identical binary oxide.¹²–¹⁴ In our earlier study, HfO₂ RRAM exhibited BRS with TiN/Ti, Ta and Pt top electrodes (TEs) but different URS with electrochemically active Cu and Ni TEs.¹⁴ Among them, the HfO₂ RRAM with Ni TEs showed excellent cycling variations, endurance, retention, and low RESET current of 50 μA.¹⁴,¹⁵ The forming and SET switching were attributed to the Ni filament formation because of the electrochemical metallization effect, i.e., Ni cations oxidized at the Ni anode migrate through HfO₂ before eventually reduced at the Si cathode. The RESET switching was attributed to the dissolution and rupture of the Ni filaments by Joule heating. However, the dependence of different binary oxides on the RS mode using an identical metal TE was less discussed. Whether or not the same type of filaments forms in different binary oxide RRAMs using the same TE requires further investigations. Therefore, the interplay between metal electrodes and binary oxides is still not completely understood.

In this study, RS modes of CMOS-compatible binary oxides including SiO₂, Al₂O₃, HfO₂, and ZrO₂ were systematically investigated using Ni TEs. Preferential BRS in amorphous Al₂O₃ and SiO₂ and URS in polycrystalline HfO₂ and ZrO₂ suggest a RS mechanism depending strongly on the binary oxide films. Backside secondary ion mass spectrometry (SIMS) confirmed substantial Ni migration in the polycrystalline HfO₂ but not in the amorphous Al₂O₃ after forming, supporting that the formation of Ni conducting filaments was responsible for the observed URS. The URS location where the connecting and rupture of conducting filaments take place at $V_{\text{SET}}$ and $V_{\text{RESET}}$ was further examined using various bilayer structures. The oxide layer next to the bottom electrode (BE) was found to play a significant role in URS. The result was in good agreement with the conical-shape Ni filament model,¹⁵,¹⁶ where the URS location was postulated to be near the BE with a smaller filament diameter.

2. Experimental Procedure

CMOS-compatible Ni/binary oxide/Si memory cells using SiO₂, Al₂O₃, HfO₂, and ZrO₂ as monolayer or bilayer RS structures were fabricated on heavily doped p⁺-Si substrates. After standard RCA clean and rapid thermal oxidation at 500 °C for 10 s in ambient O₂, four different 10-nm monolayer films, HfO₂/SiO₂ (10 nm/2–5 nm), HfO₂/Al₂O₃ (10 nm/2–5 nm), and Al₂O₃/HfO₂ (2–15 nm/10 nm) bilayer films were deposited. SiO₂ was deposited by low-pressure chemical vapor deposition at 680 °C using Si(OC₂H₅)₄ (TEOS) as the precursor. HfO₂ and Al₂O₃ were deposited by metal organic chemical vapor deposition at 500 °C using Hf(OBu)₂(mmp)₂/O₂ and Al[OCH(CH₃)₂]₃/O₂ as the precursors, respectively. ZrO₂ was deposited by atomic
layer deposition at 300°C using Zr[N(CH$_3$)$_2$C$_2$H$_5$]$_4$ (TEMAZr) and O$_2$ as the precursors, followed by post annealing at 400°C. Finally, Ni TEs with a thickness of 100 nm and a diameter of 200 μm were deposited by DC sputtering and a shadow mask process. All devices were measured using an Agilent 4156B semiconductor parameter analyzer by applying voltage to the top electrodes while the p$^+$-silicon substrates were grounded.

### 3. Results and Discussion

Figure 1 illustrates the typical RS current–voltage ($I$–$V$) characteristics of the four binary oxides with Ni TEs using DC voltage sweep. To initialize RS, a positive-polarity forming process (not shown) was necessary using a fixed current compliance of 100 μA. In Fig. 1, the HfO$_2$ and ZrO$_2$ devices showed URS with positive $V_{SET}$ and $V_{RESET}$, whereas those with SiO$_2$ and Al$_2$O$_3$ exhibited only BRS. The HfO$_2$ and ZrO$_2$ devices can also be reset at negative $V_{RESET}$ for BRS. The RS properties reported here were reproducible with at least several dozen cycles of continuous voltage sweeps. Figure 2 shows the statistical distributions of $V_{SET}$ and $V_{RESET}$ of different binary oxides, where both BRS and URS existed in the HfO$_2$ and ZrO$_2$ devices. The lack of URS in the SiO$_2$ and Al$_2$O$_3$ devices was significantly different from the coexistence of URS and BRS in the HfO$_2$ and ZrO$_2$ devices. Furthermore, the temperature-dependent LRS resistances of the Ni/Al$_2$O$_3$/Si and Ni/HfO$_2$/Si devices were measured, as shown in Figs. 3(a) and 3(b). Negative temperature coefficient of LRS in the Ni/Al$_2$O$_3$/Si device suggested a transport mechanism related to the charge hopping through semiconductive filaments. By contrast, positive temperature coefficient of LRS in the Ni/HfO$_2$/Si device exhibited typical metallic characteristics. The results implied that different compositions of conductive filaments might exist in the Ni/Al$_2$O$_3$/Si and Ni/HfO$_2$/Si devices and result in the different RS modes.

In our earlier study of the HfO$_2$-based RRAM with various TEs, 50-nm HfO$_2$ with TiN/Ti, Ta, and Pt TEs also showed preferential BRS. Oxygen-deficient filaments in HfO$_2$ were confirmed by local energy dispersive X-ray spectroscopy (EDX) and believed to be responsible for BRS. Therefore, the BRS in Ni/Al$_2$O$_3$/Si and Ni/SiO$_2$/Si might also correlate to oxygen vacancy-related filaments in the bulk of binary oxides. This is further supported by the fact that the similar preferential BRS in Al$_2$O$_3$ and SiO$_2$ was also observed using an inert Pt TE in Fig. 4, where filament compositions other than oxygen vacancy were less likely. Alternatively, the URS in Ni/HfO$_2$/Si had been attributed to the formation of metallic Ni filaments, confirmed by excessive Ni diffusion by SIMS and high-resolution transmission electron microscopy (HRTEM) from several research groups. The resembling RS characteristics of Ni/ZrO$_2$/Si suggested a similar mechanism.

Figure 5 compares the backside SIMS profiles of the Ni/Al$_2$O$_3$/Si and Ni/HfO$_2$/Si devices before and after positive forming. Backside SIMS profiling suppressed the artificial Ni knock-on effect from the Ni TEs in the conventional front-side SIMS, and allowed the investigation of the Ni filament formation in RRAMs. Some intermixing at the Ni/HfO$_2$ and Ni/Al$_2$O$_3$ interfaces was attributed to the...
sputtering process of the Ni deposition. While substantial Ni migrated from the TE into the HfO₂ layer after forming with the amount decreased gradually toward the Si BE, the Ni migration into the Al₂O₃ layer after forming was prohibited and the peak oxygen intensity in Al₂O₃ was reduced by 20% to become more oxygen deficient. Therefore, Ni filaments were believed to be formed only in HfO₂ but not in Al₂O₃ and responsible for the distinct difference in the RS mode and the temperature coefficient of LRS. The HfO₂ and ZrO₂ films used in this study were polycrystalline according to X-ray diffraction (XRD) analysis, as shown in Fig. 6. The oriented grain boundaries were suspected to allow rapid Ni migration across HfO₂ and ZrO₂. By contrast, the amorphous SiO₂ and Al₂O₃ lack of oriented grain boundaries likely suppressed Ni migration. Note that amorphous Al₂O₃ had been explored as an excellent diffusion barrier for Cu/low-κ interconnects¹⁸ and the crystallinity is generally believed to have profound impacts on the effectiveness of Cu diffusion barriers.¹⁹

Table I summarizes the interplay between TE and binary oxide materials and the corresponding RS modes in this work and in Ref. 14. According to the aforementioned physical and electrical evidence, we summarize the plausible RS mechanisms as follows: The preferential BRS may be attributed to the formation of oxygen-deficient filaments. The connecting and rupture were driven by the migration of oxygen anions using bipolar electric field. URS existed only when using electrochemically active metals of Ni and Cu as anode electrodes, accompanied by polycrystalline binary oxides of HfO₂ and ZrO₂. Because the binary oxides acted as solid electrolytes in an electrochemical cell, different crystallinities of binary oxides significantly affected the cation migration and thus the formation of metallic filaments. The URS RESET was enabled because of Joule heating and thermal dissolution of the Ni filaments.
The design of binary oxide bilayer structures can facilitate in-depth understanding on the URS location where the connecting and rupture of conducting filaments take place at \( V_{\text{SET}} \) and \( V_{\text{RESET}} \). The Ni/3-nm \( \text{Al}_2\text{O}_3/10\)-nm \( \text{HfO}_2/\text{Si} \) (NAHS) and Ni/10-nm \( \text{HfO}_2/3\)-nm \( \text{Al}_2\text{O}_3/\text{Si} \) (NHAS) devices were fabricated using an identical process except the reversed deposition sequence of \( \text{HfO}_2 \) and \( \text{Al}_2\text{O}_3 \). Both devices required a similar forming voltage of approximately 7.5 V. URS was observed in the NAHS device in contrast to preferential BRS in the NHAS device, as shown in Fig. 7. Because of the preferential BRS in \( \text{Al}_2\text{O}_3 \) and the coexistence of BRS and URS in \( \text{HfO}_2 \), the RS mode in the bilayer devices is postulated to be governed by the binary oxide layer immediately next to the BE.

It was reported that the filament morphology of the Ni/\( \text{HfO}_2/\text{Si} \) URS devices may be consistently explained by a conical-shape filament model, where the connecting and rupture of Ni filaments occurred locally near the BE with a smaller diameter.\(^{15}\) The numerical simulation of the temperature profile at \( \text{RESET} \) in a cylindrical and a conical-shape filament are shown in Fig. 8. The \( \text{RESET} \) temperature of 600 K was chosen for illustration purpose only, but agreed with the fact that the Ni filaments may be ruptured above 573 K.\(^{14}\) The temperature rise because of Joule heating was the highest at the middle of the cylindrical filament but near the BE of the conical-shape filament. Therefore, the tendency of Ni filament formation in the oxide layer next to the BE played a significant role in URS.

The thickness effect of \( \text{Al}_2\text{O}_3 \) in the NAHS and NHAS bilayer structures was also examined. Another Ni/10-nm \( \text{HfO}_2/\text{SiO}_2/\text{Si} \) (NHSS) bilayer structure with various \( \text{SiO}_2 \) thicknesses was also fabricated for comparison. All structures demonstrated high-yield BRS. Additionally, Fig. 9 shows the device yield of URS in all bilayer structures. The yield device was defined allowing at least five consecutive unipolar RS cycles, and total 50 devices were measured for each structure.

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thin SiO}_2 might allow the formation of Ni filaments and URS. The strong dependence of the SiO}_2 thickness between the Si BE and HfO}_2 also explains stable URS in Ni/HfO}_2/Si, where a thin interfacial layer of SiO}_2 (about 1.5 nm) existed between HfO}_2 and Si, whereas only BRS existed in the aforementioned 10-nm SiO}_2 monolayer.

Figure 10(a) depicts a RS model where the composition of the filament in bilayer structures depends on the metal cation diffusivity in binary oxides. For the NHAS device, Ni ions diffuse into polycrystalline HfO}_2 through grain boundaries before eventually blocked by the amorphous Al}_2O}_3 barrier during the forming and SET process. Hence, the dominant composition of conducting filaments was Ni in HfO}_2. However, further investigations would be necessary to exclude the possibility of rupturing the Ni filaments in HfO}_2 under bipolar RESET driven by electric field. For the NAHS device with a thinner Al}_2O}_3 layer, sufficient Ni ions were able to diffuse through thin Al}_2O}_3 into HfO}_2 because of the abundant source, and formed conical-shape Ni filaments necessary for URS. However, the filament size regulated by the top Al}_2O}_3 layer is expected to be smaller in the NAHS device as compared to that in the Ni/HfO}_2/Si monolayer device. This is further supported by the tighter distribution of HRS resistance (R}_BRS), LRS resistance (R}_LRS), V}_SET, and V}_RESET of the NAHS bilayer device, as shown in Figs. 10(b) and 10(c). The higher R}_LRS and lower R}_BRS are the signature of the reduced filament size because of the increase of filament resistance at LRS and residual small filaments at HRS that were unable to be completely ruptured because of insufficient RESET power.

4. Conclusions

The RS modes of binary oxides, including SiO}_2, HfO}_2, Al}_2O}_3, and ZrO}_2, were investigated using Ni TEs. URS in HfO}_2 and ZrO}_2 correlated with metallic Ni filaments, whereas preferential BRS in Al}_2O}_3 and SiO}_2 correlated with oxygen-deficient filaments. The composition difference of the conducting filaments was confirmed by the backside SIMS analysis, showing the suppression of Ni migration in amorphous Al}_2O}_3 as compared to that in polycrystalline HfO}_2. Furthermore, the RS mode can be further tailored using bilayer structures. The NHAS bilayer structure displayed BRS only, but the NAHS bilayer with thinner Al}_2O}_3 was capable of URS. The absence of URS in the NHAS structure implies that the filament connecting and rupture occurred locally near the Si BE for URS, in support of the conical-shape Ni filament model. Additionally, the thickness effect of the Al}_2O}_3 and SiO}_2 interfacial layers in the bilayer structures can be consistently explained by Ni migration. The results suggest new possibilities of designing the RS mode using engineered interfacial layers between binary oxides and metal electrodes.

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