



# Reversible transition of resistive switching induced by oxygen-vacancy and metal filaments in $\text{HfO}_2$



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## ARTICLE INFO

### Article history:

Received 8 February 2013

Received in revised form 11 June 2013

Accepted 12 August 2013

Available online 5 September 2013

The review of this paper was arranged by Dr. Y. Kuk

### Keywords:

RRAM

Filament

Multi-level-cell

Resistive switching

## ABSTRACT

In contrast to the irreversible transition of resistive switching induced by oxygen-vacancy filaments (VF) and metal filaments (MF) reported in the literature, this study reports coexistence and completely reversible transition of VF- and MF-induced resistive switching in a  $\text{Ni}/\text{HfO}_2/\text{SiO}_x/\text{p}^+\text{-Si}$  device with three distinct and stable resistance states. In a dual filament model proposed, VF and MF may coexist at the same percolation path, and the formation and rupture proceed in a two-step fashion by choosing appropriate SET/RESET conditions. Exploiting the dependence of different filament compositions on resistive switching may enable new design space for future multi-level-cell resistive-switching memory.

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## 1. Introduction

Bias-dependent variable resistance in resistive-switching random access memory (RRAM) has been explained by the connection and rupture of conductive filaments in metal oxides [1–3]. Depending on material combination of a large variety of metal oxides and electrodes, filament compositions are generally classified into two categories: metal filament (MF) comprising metal precipitation from electrochemically active electrodes, such as Ni, Cu, and Ag [1,2], and oxygen-vacancy filament (VF) generated by redox of metal oxides [1,3]. However, coexistence of these two filaments in the same RRAM cell was less discussed. Jeong et al. [4] first reported coexistence of bipolar and unipolar resistive switching (RS) in a  $\text{TiO}_2$  RRAM cell by controlling current compliance ( $I_{\text{comp}}$ ) at SET. The transition from bipolar RS with low  $I_{\text{comp}}$  to unipolar RS with high  $I_{\text{comp}}$  was irreversible. Similar results were also reported in a  $\text{ZnO}$  RRAM cell [5]. More recently, Raghavan et al. [6] showed that VF and MF can coexist in a  $\text{NiSi}/\text{HfO}_2/\text{Si}$  stack, but the transition from VF-induced bipolar RS mode to MF-induced unipolar RS mode was also irreversible. Our previous study also revealed that the filament composition and RS mode in  $\text{HfO}_2$  RRAM was determined by top electrode (TE) material and voltage polarity at electrical forming [7].

This study reports coexistence and completely reversible transition of RS induced by VF and MF in a  $\text{Ni}/\text{HfO}_2/\text{SiO}_x/\text{p}^+\text{-Si}$  RRAM cell. This not only led to a better understanding on the interplay of two different filaments during RS, but also enabled new design space for multi-level-cell (MLC) implementation, which is extremely critical for ultra high-density storage. In contrast to the reported MLC RRAM in the literature utilizing only a single RS mechanism [8,9], exploiting the dependence of different filament compositions on RS properties, namely VF with higher resistance favors bipolar RS and MF with lower resistance favors unipolar RS, well-defined and stable multiple resistance states were successfully realized.

## 2. Experimental procedures

$\text{Ni}/\text{HfO}_2/\text{SiO}_x/\text{p}^+\text{-Si}$  memory cells were fabricated on heavily doped  $\text{p}^+\text{-Si}$  wafers using a contact-hole structure with an area of  $100\ \mu\text{m}^2$ . A 30-nm  $\text{HfO}_2$  layer was deposited by metal organic chemical vapor deposition at  $500\ ^\circ\text{C}$  using  $\text{Hf}(\text{OtBu})_2(\text{mmp})_2$  and  $\text{O}_2$  as precursors. Ni TEs with a thickness of 100 nm were defined by sputtering and lift-off processes. The  $\text{HfO}_2$  layer was polycrystalline and there existed a thin interfacial layer of  $\text{SiO}_x$  (about 1.5 nm) between  $\text{HfO}_2$  and Si according to previous X-ray diffraction (XRD) and transmission electron microscopy (TEM) analysis, respectively [7]. The devices were measured by applying voltage to the Ni TEs while the  $\text{p}^+\text{-Si}$  substrates were grounded as the bottom electrodes (BE). To initialize RS in the device, a negative forming voltage with  $I_{\text{comp}}$  of  $10\ \mu\text{A}$  was applied to induce

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dielectric breakdown, where oxygen vacancies generated at strong electric field formed percolation paths of VF [7]. The negative forming voltage was chosen to prevent excessive Ni migration from the TE triggered by positive forming voltage. High positive forming voltage typically accompanies with large charge-dissipation (overshoot) current, and thus results in excessive forming power and Ni migration, difficult to be completely removed at RESET [10]. This would increase the difficulty of realizing stable VF-induced RS with low switching current and reversible transition between MF-induced RS and VF-induced RS, as will be discussed in more details below.

### 3. Results and discussion

Three RS modes can be operated independently after forming using appropriate  $I_{\text{comp}}$  at SET voltage ( $V_{\text{SET}}$ ) and the polarity of RESET voltage ( $V_{\text{RESET}}$ ), as shown in the typical RS current–voltage ( $I$ – $V$ ) curves in Fig. 1. In Mode-I RS, a high resistance state (HRS) with a resistance of  $10^9$ – $10^{11} \Omega$  was switched to a low resistance state (LRS) with a resistance of  $10^6$ – $10^7 \Omega$  using positive  $V_{\text{SET}}$  and low  $I_{\text{comp}} < 50 \mu\text{A}$ . The resistances of HRS and LRS were measured at 0.2 V. The resistance ratio between HRS and LRS was larger than 100. Resetting the device back to HRS was only possible using negative  $V_{\text{RESET}}$  but not positive  $V_{\text{RESET}}$ . The first RESET event after the negative forming, as shown in Fig. 2(a), was thought to be triggered by the remnant oxygen in the Ni electrode because of its high oxygen solubility and low affinity [11]. Although negative  $V_{\text{SET}}$  and  $V_{\text{RESET}}$  can also be used for RS, this unipolar mode had limited endurance after exhausting the oxygen reservoir in the Ni electrode, and was considered unstable. The preferred bipolar RS with positive  $V_{\text{SET}}$  and negative  $V_{\text{RESET}}$  was consistent with the VF model in  $\text{HfO}_2$  RRAM [6,7], where the connection and rupture of VF are facilitated by the drift of oxygen ions under bipolar electric field using the TE/ $\text{HfO}_2$  interface as an oxygen reservoir. The LRS of Mode I is therefore also referred to as LRS(VF) in this study. To completely exclude the role of Ni migration in Mode-I RS, the RS characteristics in another  $\text{Pt}/\text{HfO}_2/\text{SiO}_x/\text{p}^+\text{-Si}$  device involving only VFs was compared in Fig. 2(b). The preferred bipolar RS in  $\text{Ni}/\text{HfO}_2/\text{SiO}_x/\text{p}^+\text{-Si}$  using low  $I_{\text{comp}}$  resembled that in  $\text{Pt}/\text{HfO}_2/\text{SiO}_x/\text{p}^+\text{-Si}$ , supporting the VF model. Furthermore, the negative temperature dependence of LRS(VF) resistance shown in Fig. 3 is consistent with the measured results of VF devices in Ref. [7]. The conduction mechanism of VF is reported to be related to charge hopping through oxygen vacancies [12,13].

In Mode-II RS as shown in Fig. 1(b), positive  $V_{\text{SET}}$  with  $I_{\text{comp}} > 1 \text{ mA}$  triggered the second RS event from LRS(VF) to a new LRS with even lower resistance of  $10^3$ – $10^4 \Omega$ . The resistance ratio in Mode II was also larger than 100. RESET may be carried out by either negative or positive  $V_{\text{RESET}}$ , i.e. both bipolar and unipolar RS existed. Significantly different from the RS in Mode I, the coexistence of stable bipolar and unipolar RS with much smaller

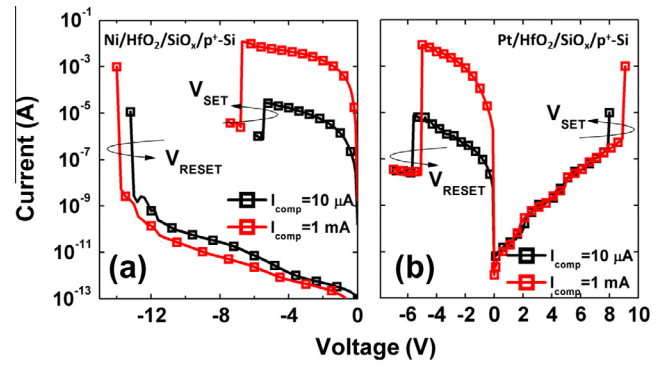


Fig. 2. (a) First RESET curves of the  $\text{Ni}/\text{HfO}_2/\text{SiO}_x/\text{p}^+\text{-Si}$  device after negative forming and (b) typical bipolar RS  $I$ – $V$  curves of the  $\text{Pt}/\text{HfO}_2/\text{SiO}_x/\text{p}^+\text{-Si}$  device.

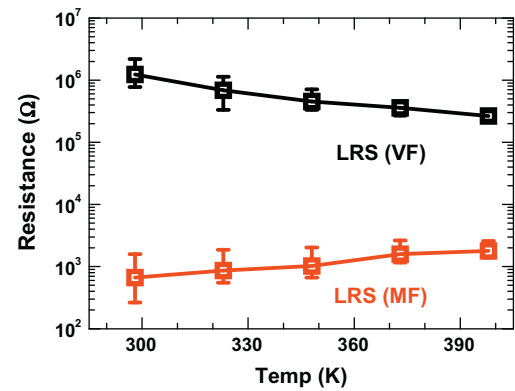


Fig. 3. Temperature dependence of the LRS(MF) and LRS(VF) resistance in  $\text{HfO}_2$  RRAM.

$V_{\text{SET}}/V_{\text{RESET}}$  and lower resistance values was attributed to the MF formation [7]. Ni migration and filament formation in a similar structure and operation conditions have been confirmed by back-side secondary ion mass spectrometry (SIMS) in our previous publication [7] and TEM by other research groups [6]. Substantial Joule heating at Mode II played a much significant role in the connection and rupture of MF, and enabled lower switching voltages and unipolar RS. The new LRS in Mode II RS is therefore also referred to as the LRS(MF) in this study. The MF model is further supported by the facts that the Mode-II RS was completely lacking in both the  $\text{Ni}/\text{HfO}_2/\text{SiO}_x/\text{p}^+\text{-Si}$  device prior to positive SET in Fig. 2(a) and the  $\text{Pt}/\text{HfO}_2/\text{SiO}_x/\text{p}^+\text{-Si}$  device without Ni filaments in Fig. 2(b) using high  $I_{\text{comp}}$ . Positive temperature dependence of resistance shown in Fig. 3 agrees on the metallic nature of the conducting filaments. Although both negative or positive  $V_{\text{RESET}}$  can be used, positive  $V_{\text{RESET}}$  was favorable to reset the device from LRS(MF) back to

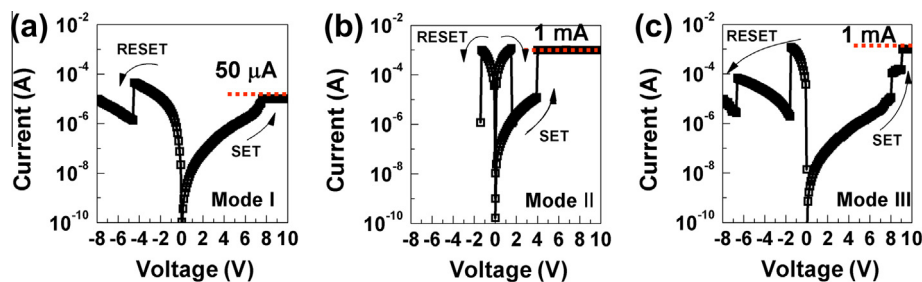


Fig. 1. Typical (a) Mode-I bipolar RS, (b) Mode-II bipolar/unipolar RS, and (c) Mode-III bipolar RS  $I$ – $V$  curves of  $\text{HfO}_2$ . The compliance current at Mode-I, Mode-II, and Mode-III were  $50 \mu\text{A}$ ,  $1 \text{ mA}$ , and  $1 \text{ mA}$ , respectively.

LRS(VF), while negative  $V_{\text{RESET}}$ , if not chosen appropriately, may reset the device completely back to HRS through sequential Mode-II and Mode-I RESET.

In Mode-III RS as shown in Fig. 1(c), Mode-I and Mode-II RS were combined to switch the device between HRS and LRS(MF) via the intermediate state of LRS(VF). The resistance ratio in Mode III was the largest (about  $10^5$ ). Positive  $V_{\text{SET}}$  with  $I_{\text{comp}} > 1$  mA led to first the VF formation, followed by the MF formation in a two-step SET process. This was supported by the two-step current increase and the existence of the intermediate LRS(VF). Note that occasionally LRS(VF) cannot be easily observed during the SET transition because the inherent smaller  $V_{\text{SET}}$  and the rapid MF formation process. If  $I_{\text{comp}}$  is set between  $50 \mu\text{A}$  and  $1$  mA, both Mode-I and Mode-III RS may occur in a less deterministic fashion. The device can be switched back to HRS by rupturing both MF and VF sequentially in a two-step RESET process using negative  $V_{\text{RESET}}$ . Because  $V_{\text{RESET}}$  of LRS(MF) was smaller than  $V_{\text{RESET}}$  of LRS(VF), the intermediate LRS(VF) was much easily observed during the RESET transition.

Although the connection and rupture of VFs and MFs were believed to be responsible for Mode-I and Mode-II RS, respectively, both VF and MF might locate at the same percolation path in a dual filament model. In this study, by suppressing Ni migration at forming and at Mode-I SET, VFs were the only preexisting current paths at LRS(VF) and therefore the most likely percolation paths of MFs in Mode-II RS because of the positive feedback between Joule heating and the accompanying electrochemical reaction/ion migration. In addition to  $I_{\text{comp}}$ , it is speculated that interfacial  $\text{SiO}_x$  might play a crucial role in the coexistence of Mode-I and Mode-II RS. Our previous backside SIMS analysis showed that Ni electromigration was enhanced in polycrystalline oxides but retarded in amorphous oxides [14]. Furthermore, insertion of amorphous  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2$  layers between  $\text{HfO}_2$  and the Si BE was found to favor bipolar RS and prohibit unipolar RS [14]. During MF formation, Ni cations dissolved from the anode (TE) migrated through the dielectric and reduced at the cathode. The reduced Ni precipitation at the cathode served as a virtual cathode that decreased the effective distance between the anode and cathode and facilitated the positive feedback of MF formation. When the SET power was insufficient with low  $I_{\text{comp}}$ , the  $\text{SiO}_x$  interfacial layer served as a Ni barrier and suppressed the Ni reduction at the cathode. This may explain that only VFs were formed at Mode-I SET.

Fig. 4(a) and (b) shows the statistical  $V_{\text{SET}}$ ,  $V_{\text{RESET}}$ , and bi-stable resistance distributions of 100 consecutive RS cycles for each mode.  $V_{\text{SET}}$  and  $V_{\text{RESET}}$  in Mode II was significantly smaller than

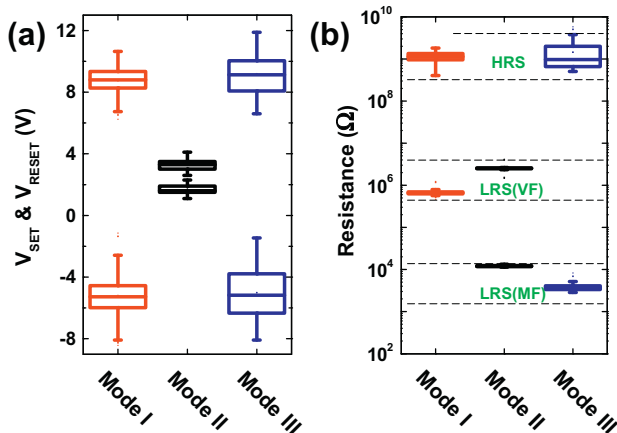


Fig. 4. Statistical distribution of (a) switching voltages and (b) bi-stable resistance in the three different RS modes. At least one hundred switching cycles were measured for each mode. Three distinct resistance states, HRS, LRS(VF), and LRS(MF), can be observed.

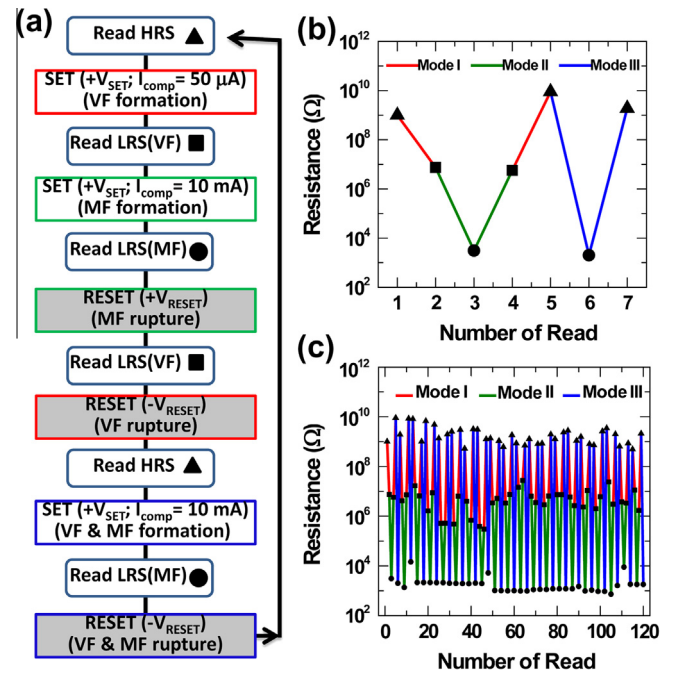


Fig. 5. (a) Test sequence demonstrating completely reversible transition among Mode-I, Mode-II, and Mode-III RS by adjusting  $I_{\text{comp}}$  and  $V_{\text{RESET}}$  polarity. Multilevel resistance of three independent states, HRS, LRS(VF), and LRS(MF), using a single cycle and multiple cycles of the test sequence in (a) are shown in (b) and (c), respectively.

those in Mode I and Mode III, and stable unipolar RS was only possible in Mode II. HRS, LRS(VF), and LRS(MF) all exhibited tight resistance distributions regardless of the RS mode. Future optimization to reduce the operation voltages of Mode I and Mode III involving VFs would be helpful for low-voltage applications. Finally, to demonstrate completely reversible transition among the three RS modes for the MLC applications, a test sequence, Mode-I SET, Mode-II SET, Mode-II RESET, Mode-I RESET, Mode-III SET, and Mode-III RESET as shown in Fig. 5(a), was utilized by adjusting  $I_{\text{comp}}$  and  $V_{\text{RESET}}$  polarity. The device can be successfully switched among the three independent resistance states reversibly, as shown in Fig. 5(b) and (c).

#### 4. Conclusion

Although distinct RS modes induced by VF and MF have been shown to coexist in  $\text{HfO}_2$  RRAM in the literature, the transition between these two RS modes were long thought to be irreversible. By suppressing excessive Ni migration at electrical forming in a  $\text{HfO}_2$  RRAM with Ni TE, this study shows that VF and MF can coexist at the same percolation path in a two-step SET process, where the MF formation is facilitated by the preexisting VF in a dual filament model. A reversed sequence can be utilized to rupture MF first using Joule heating and then VF at strong electric field in a two-step RESET process. Furthermore, the  $\text{HfO}_2$  RRAM can be reversibly switched among three distinct states with significant difference in resistance by choosing appropriate operation conditions. The better understanding on the coexistence and reversible transition of RS induced by VF and MF may open up new opportunities for future high-density MLC RRAM.

#### Acknowledgements

This work was supported by National Science Council of Taiwan, Republic of China, under grant NSC 100-2628-E-009-025-MY2, 101-2221-E-009-089-MY3, and CTSP 100RB13. The

authors would like to thank the Nano Facility Center at National Chiao Tung University and National Nano Device Laboratories, where the experiments in this paper were performed.

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