

Overcoming the Endurance-Retention Trade-Off in CBRAM: the Introduction of Co as Active Electrode

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Abstract

We report an overview of the limitations of CBRAM devices in the sub-100 μ A regime. We demonstrate that these limitations can be overcome by introducing Co as active electrode, extending the endurance lifetime and the data retention. We further provide guidelines to boost the memory performances by engineering the switching electrode. These results demonstrate that Co-based CBRAM represent a breakthrough in the low-power RRAM landscape.

1. CBRAM limitation in the sub-100 μ A regime

The switching mechanism of Conductive-Bridging RAM (CBRAM) devices is based on the voltage-induced electrochemical formation and dissolution of a metallic filament [1]. Its structure is made of a solid electrolyte (or switching layer) sandwiched between an electrochemically active electrode (typically Cu or Ag) and an inert electrode. Within the very wide spectrum of Resistive Random-Access Memories (RRAM), Conductive-Bridging RAM (CBRAM), as better variability and much larger memory window (MW) have been demonstrated with respect to oxygen-vacancy based RRAM (OxRAM) in low-current ($< 100 \mu\text{A}$) regimes [2,3]. However, all CBRAM devices are affected by a negative correlation between the endurance lifetime and the data retention, preventing the optimization of both reliability aspects in the same device [4,5]. Moreover, they experience a strong degradation of the filament stability in the sub-100 μ A regime, especially for Ag active electrode, which is thus mostly used for selector applications (Volatile Conductive Bridge) [6]. In addition, the potential scalability of Cu-based devices is hindered by the corrosion induced by Cl-plasma gases commonly used for reactive ion etch (RIE) [7]. We recently demonstrated that Co shifts the endurance/retention trade-off to better performances [4]. Co is also more robust to RIE and is a well-known material widely used for interconnects. Here we provide a detailed description of the performance boost induced by the introduction of Co, and we offer additional pathways for enhancing the Co-based CBRAM performances by engineering the switching layer.

2. Benefits of Co as active electrode

We selected Co based on its oxidation potential, its ion radius, and the cohesive energy [4], which is higher than the one of Cu and Ag. This suggests a better filament stability when the same switching layer is used. To demonstrate this, we benchmarked Co against Cu as active electrodes in stacks with Al_2O_3 or HfO_2 as switching layer (fig. 1). The comparison clearly shows that Co ensures lower forming voltage (fig. 1a) and better filament stability for an operating

current $I_{\text{OP}} = 50 \mu\text{A}$ (fig. 1b), leading to a larger memory window (fig. 1c).

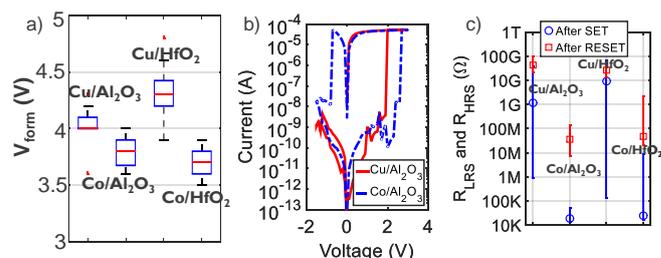


Figure 1: (a) Forming voltage V_{form} for Al_2O_3 - and HfO_2 -based stacks with Co and Cu as active electrodes; (b) I-V switching characteristics comparing Co to Cu with Al_2O_3 as switching layer; (c) LRS and HRS extracted for Co- and Cu-based device with Al_2O_3 and HfO_2 as switching layers.

Interestingly, to induce a stable filament and a large memory window for $I_{\text{OP}} = 10 \mu\text{A}$, extensive cycling is necessary (fig. 2a). By applying the QPC model to CBRAM devices, we demonstrated that the number of atoms in the filament increases with cycling, therefore improving the filament stability (fig. 2b).

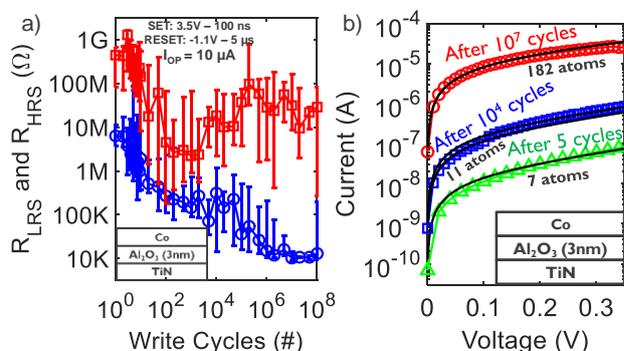


Figure 2: (a) Endurance characteristics of $\text{Co}/\text{Al}_2\text{O}_3$ -based devices (switching conditions are reported in the inset); (b) QPC extraction of the number of atoms in the narrowest part (constriction) of the Co filament at 3 stages of the endurance tests in fig. 2a.

We also showed that cycling is beneficial for the data retention, thanks to the increased number of atoms in the filament [4]. Considering the impact of cycling on endurance and retention, we propose to engineer the switching layer to enhance the Co ion conductivity, ensuring strong Co injection and thus a stable filament in the first switching cycles.

3. Co-based CBRAM: Switching-Layer engineering

As Cu transport is reported to be facilitated by the presence of hydroxyl groups [8], and the same is expected for Co, we proposed hygroscopic oxides as switching layers for enhancing the Co filament stability [4]. We selected LaSiO

and we gradually decreased the hygroscopicity by performing anneals at different pressures (fig. 3a). We demonstrate that both the AC cycling and the data retention are strongly affected by the anneals. With the non-annealed sample, $>10^7$ cycles with $MW>100x$ are achieved by applying very low-energy pulses of 2.5V/100-ns (fig. 3b). With the annealed sample, the SET operation tends to fail during the cycling test. The anneal also deteriorates the data retention (fig. 3c). We recently demonstrated that better endurance and retention are mainly driven by the higher amount of polar La-OH bonds [9], due to the strong dipole attraction between the Co ions and the partial charge developed on the OH group. Therefore, increasing the amount of polar La-OH bonds may further improve the Co/LaSiO-based CBRAM reliability.

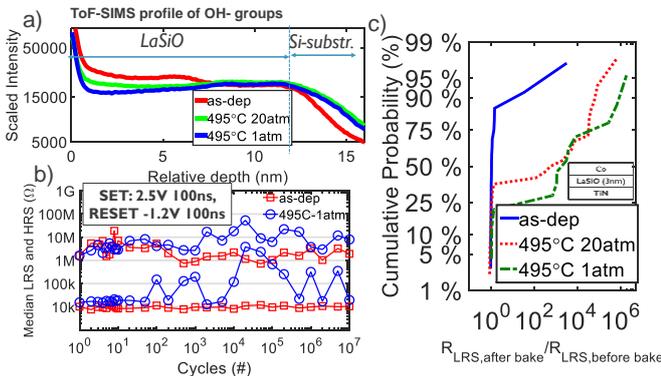


Figure 3: (a) Time-of-Flight Secondary Ion Mass Spectroscopy (ToFSIMS) of OH⁻ groups in LaSiO layers annealed at 495 °C at different temperatures; (b) Comparison of endurance characteristics of Co-based devices using annealed and non-annealed LaSiO switching layers; (c) retention benchmarking for the 3 LaSiO layers.

An alternative solution for enhancing the Co-filament stability is the adoption of chalcogenides as switching layers. Chalcogenides have been used since the early stages of CBRAM development thanks to their high ion conductivity. We selected GeSe considering the optimal data retention we had demonstrated with Cu active electrode [10].

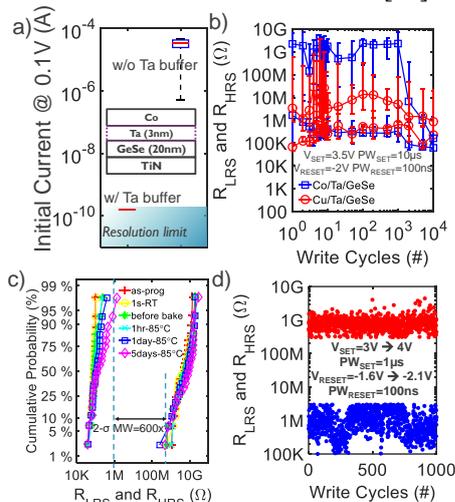


Figure 4: (a) Suppression of the pristine current by inserting a Ta buffer layer between Co and GeSe; (b) Endurance characteristics benchmarking of Cu and Co with the same Ta/GeSe-based stack; (c) Retention characteristics of Co/Ta/GeSe devices with corresponding verified cycling test (d).

By inserting a metal buffer between Co and GeSe we ensured extremely low pristine current (fig. 4a), and we demonstrated that Co leads to a larger MW than Cu (fig. 4b). With Co/Ta/GeSe stacks, excellent retention (fig. 4c) can be combined with a 100x memory window programmed for 10^3 cycles, by using to a program-verify algorithm (fig. 4d).

We thus show that by engineering the CBRAM stack different application domains can be targeted: hygroscopic oxides are suitable where fast/low-voltage switching and long endurance lifetime is necessary, while Co/Ta/GeSe-based stacks are an excellent solution for long retention devices.

We summarize the endurance and retention data we collected on Cu-based and Co-based devices in fig. 5. While an endurance-retention trade-off is to be pursued for both device classes, for Co-based devices this trade-off is shifted toward higher performances.

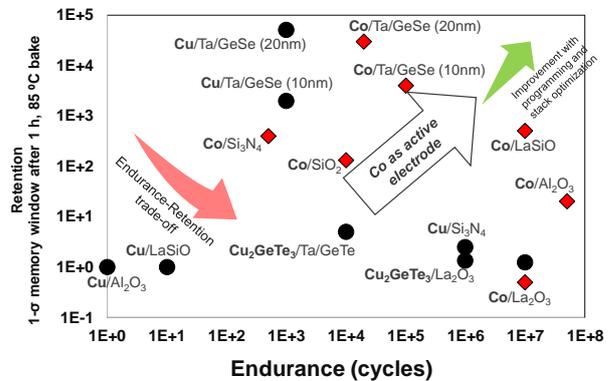


Figure 5: Endurance and Retention benchmarking for different Cu-based and Co-based CBRAM stacks.

Conclusions

We outlined the main limitations affecting CBRAM devices when the operating current is reduced. We demonstrated that by replacing Cu with Co the filament stability is strongly improved, ensuring large memory window ($>10^3x$) for $I_{OP}=50\mu A$, and that the endurance/retention trade-off in Co-based CBRAM can be improved by accurately selecting the switching layer. With this study, we show that Co shifts the endurance-retention trade-off toward higher performances, and that the CBRAM reliability can be tailored for different applications by engineering the stack.

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