

# Recovery of ferroelectric property after endurance test by positive reset voltage application for CeO<sub>x</sub>-capped ferroelectric HfO<sub>2</sub> films

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## Abstract

The influence of CeO<sub>x</sub> capping on HfO<sub>2</sub> films on the ferroelectric property is investigated. An improved switching endurance was found with the capping, but a fatigue effect appeared. A better breakdown only in the negative voltage application indicates the movement of oxygen ions in the capped layer to the underlying HfO<sub>2</sub> layer. A slight recovery with a better endurance property was obtained by applying a negative voltage among the switching pulses.

## 1. Introduction

Ferroelectric HfO<sub>2</sub> films have attracted considerable attention owing to their scalability below 10 nm thickness [1]. Reliability issues, however, including switching endurance, wake-up, or fatigue effects, remain. The ferroelectric property in HfO<sub>2</sub> films is influenced by oxidation time during atomic layer deposition (ALD) processes; thus, the control of the oxygen vacancy (V<sub>O</sub>) concentration in HfO<sub>2</sub> films is essential [2,3]. Recently, an improvement in the endurance by CeO<sub>x</sub> capping on Y-doped HfO<sub>2</sub> (Y:HfO<sub>2</sub>) films was reported [4]. The capping function is reported to supply or absorb O atoms to the underlying HfO<sub>2</sub> layer to control the V<sub>O</sub> concentration in the HfO<sub>2</sub> layer [5]. However, a detailed analysis of the reliability is not clarified yet. In this study, we show that oxygen ion (O<sup>2-</sup>) movement in the capped layer may be the origin for better endurance and the appearance of the fatigue effect.

## 2. Device structure

Metal-insulator-metal (MIM) capacitors were fabricated on an n<sup>+</sup>Si substrate with bottom and top W electrodes. 7.5-nm-thick Y:HfO<sub>2</sub> films were all deposited by ALD using tetrakis-dimethylamino hafnium (TDMAH), tris-isopropyl-cyclopentadienyl yttrium (iPrCp)<sub>3</sub>Y, and precursors. The doping concentration in the Y:HfO<sub>2</sub> layer is designed to be 5 mol%. The capped CeO<sub>x</sub> layer with a thickness of either 0.6, 1, or 2 nm was deposited by tris-ethyl-cyclopentadienyl cerium (EtCp)<sub>3</sub>Ce precursor. The MIM capacitors were annealed at 500°C for 1 min or 100 min in a forming gas (3%H<sub>2</sub>+97%N<sub>2</sub>) atmosphere.

## 3. Ferroelectric property and endurance with CeO<sub>x</sub>-capping

The MIM capacitor, annealed for 1 min, showed better ferroelectric hysteresis loops when the capping thickness is more than 0.6 nm (fig. 1). Annealing for a long period (100 min) further increases the ferroelectricity, but the capping still has the advantage (fig. 2).

Switching cycle test at V<sub>pp</sub>=4V revealed a wake-up effect for non-capped capacitor and showed breakdown

before 10<sup>8</sup> cycles. The capped capacitor, on the other hand, showed a reduced wake-up effect but with a fatigue effect once the switching cycle exceeds 10<sup>6</sup> times. The breakdown occurred before 10<sup>10</sup> cycles, a significant improvement to the non-capped capacitor (fig.3). The DC current is measured regularly among the cycling test and is shown in fig. 4. Note that 0.5 V includes the switching current component and 1.5 V is the leakage component. A gradual current decrease at 0.5 V for capped capacitor indicates the reduction of P<sub>r</sub> along with the cycle test. We can confirm that the suppressed leakage current contributes to the prolonged endurance. The effect is more pronounced for lower switching voltage (V<sub>pp</sub>=3.6V).

The breakdown measurements of the MIM capacitors are shown in fig. 5. While no difference was found in the positive voltage application, a larger breakdown voltage was obtained in the negative direction with the capping. As the oxygen ion conductivity of CeO<sub>x</sub> is known to be large [6], one can suspect that O<sup>2-</sup> ions drift to the underlying HfO<sub>2</sub> layer to compensate for the created V<sub>O</sub> filament in the layer (fig. 6 (a)). Besides the compensation of the V<sub>O</sub> in the HfO<sub>2</sub> layer, the O<sup>2-</sup> ions may pin the ferroelectric domain wall and might be the reason for the fatigue effect (fig. 6 (b)).

## 4. Recovery of ferroelectricity with negative voltage

A reset voltage (V<sub>reset</sub>) was applied to the capped capacitor after switching of 10<sup>8</sup> times. We observed a recovery in the ferroelectric property when a V<sub>reset</sub> of 2 V was used (fig. 7). By applying a V<sub>reset</sub> for every 10<sup>6</sup> cycles, the fatigue effect was found to be suppressed (fig. 8). The impact of the positive V<sub>reset</sub> is hypothesized to the extraction of O<sup>2-</sup> as well as electrons trapped at CeO<sub>x</sub>/HfO<sub>2</sub> interface.

## 5. Conclusion

The effect of CeO<sub>x</sub> capping on Y:HfO<sub>2</sub> layer on the ferroelectric properties is investigated. Improvement in ferroelectricity with better endurance was obtained. The effect is presumably due to the oxygen ion movement in the CeO<sub>x</sub> to compensate for the V<sub>O</sub> in the HfO<sub>2</sub> layer. The fatigue effect can be considered to be the O<sup>2-</sup> and electrons to pin the domain. Applying a positive reset voltage among the cycling test recovers the ferroelectricity, unpin the domains.

## Acknowledgment

The work was supported by JST COI Gran Number JPMJCE1309. One of the authors, K. M., was supported by The FUTABA Foundation.

**References**

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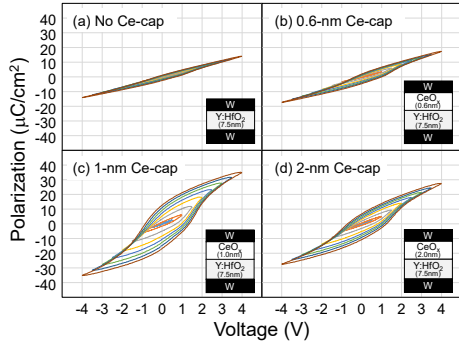


Fig. 1 Hysteresis loops with different CeO<sub>x</sub>-capping layer thicknesses.

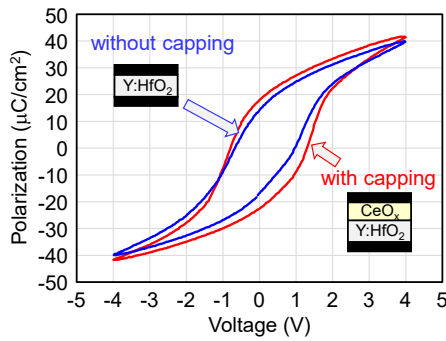


Fig. 2 Hysteresis loops with capacitors annealed at 500°C for 100 min.

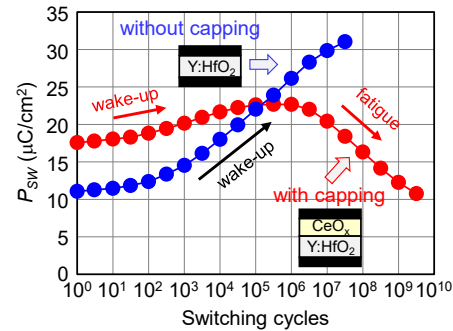


Fig. 3 Switching endurance under  $V_{pp}=2$  V at 500 kHz.

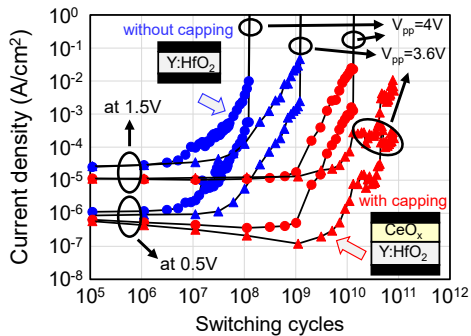


Fig. 4 Current ( $J$ ) measured during switching cycles. Note that  $J$  at 0.5 V includes the switching current component and  $J$  at 1.5 V is the leakage current.

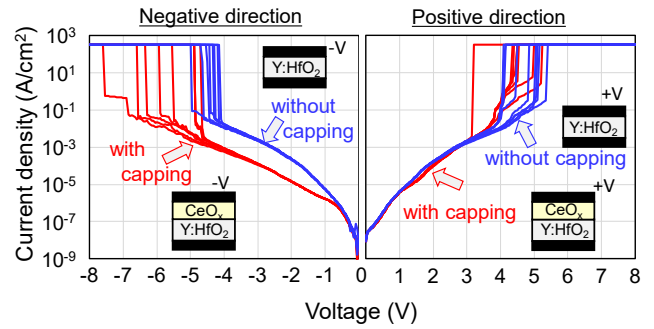


Fig. 5 Breakdown measurement of the capacitors for both negative and positive directions.

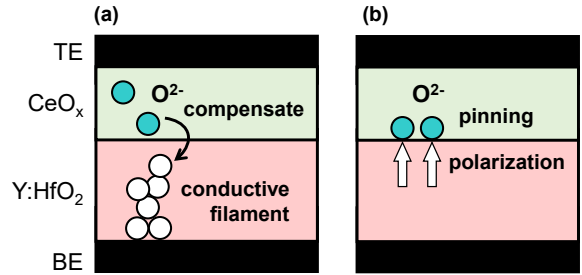


Fig. 6 (a) O<sup>2-</sup> ions in the capping layer compensate the V<sub>O</sub> in the HfO<sub>2</sub> layer to prevent from breakdown. (b) O<sup>2-</sup> ions can pin the ferroelectric domain to decrease the ferroelectricity.

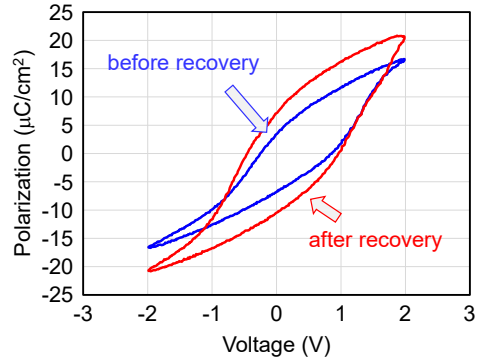


Fig. 7 Recovery of the ferroelectricity with positive  $V_{reset}$  application. ( $V_{reset}=2$  V for 1 s)

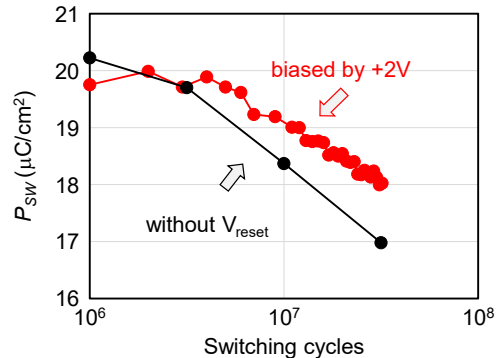


Fig. 8 Relaxed fatigue effect with positive  $V_{reset}$  for every  $10^6$  cycles.