Enhanced remnant polarization in $Hf_{0.5}Zr_{0.5}O_2$ capacitor by introducing transition metal dichalcogenides capping layer

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Abstract

$Hf_{0.5}Zr_{0.5}O_2$ (HZO) is a promising material for applications to ferroelectric (FE) nanoscale devices, such as ferroelectric random access memory (FeRAM) and FE field effect transistors (FEFET), owing to its down-scaling capability and CMOS compatibility. However, its experimental remnant polarization ($2P_r$) exhibits relatively low value compared to conventional FE materials. Meanwhile, high-performance nonvolatile FE memory requires high $2P_r$ characteristics to achieve a large memory window in the device [1]. It is widely believed that ferroelectric properties of HZO thin films are originated from its orthorhombic phase (o-phase). To stabilize the ferroelectric o-phase, introducing a capping layer with lower thermal expansion coefficient than HZO to apply tensile stress is a prospective method.

Here, we introduce a novel capping layers of transition metal dichalcogenides (TMDs), specifically MoS_2, and WS_2, deposited via pulsed laser deposition on atomic layer deposited HZO thin films. Notably, HZO thin films with few layer MoS_2 and WS_2 exhibit enhanced remanent polarization of $2P_r \approx 30\ \mu C/cm^2$ and $20\ \mu C/cm^2$, respectively, which is three-times, and two-times higher than that of bare HZO thin films ($2P_r \approx 10\ \mu C/cm^2$). Furthermore, TMDs-capped HZO thin films show long retention (>10^5 seconds). The enhancement in ferroelectric properties may be attributed to TMDs-induced stabilization of the o-phase, facilitated by an enlarged clamping effect.

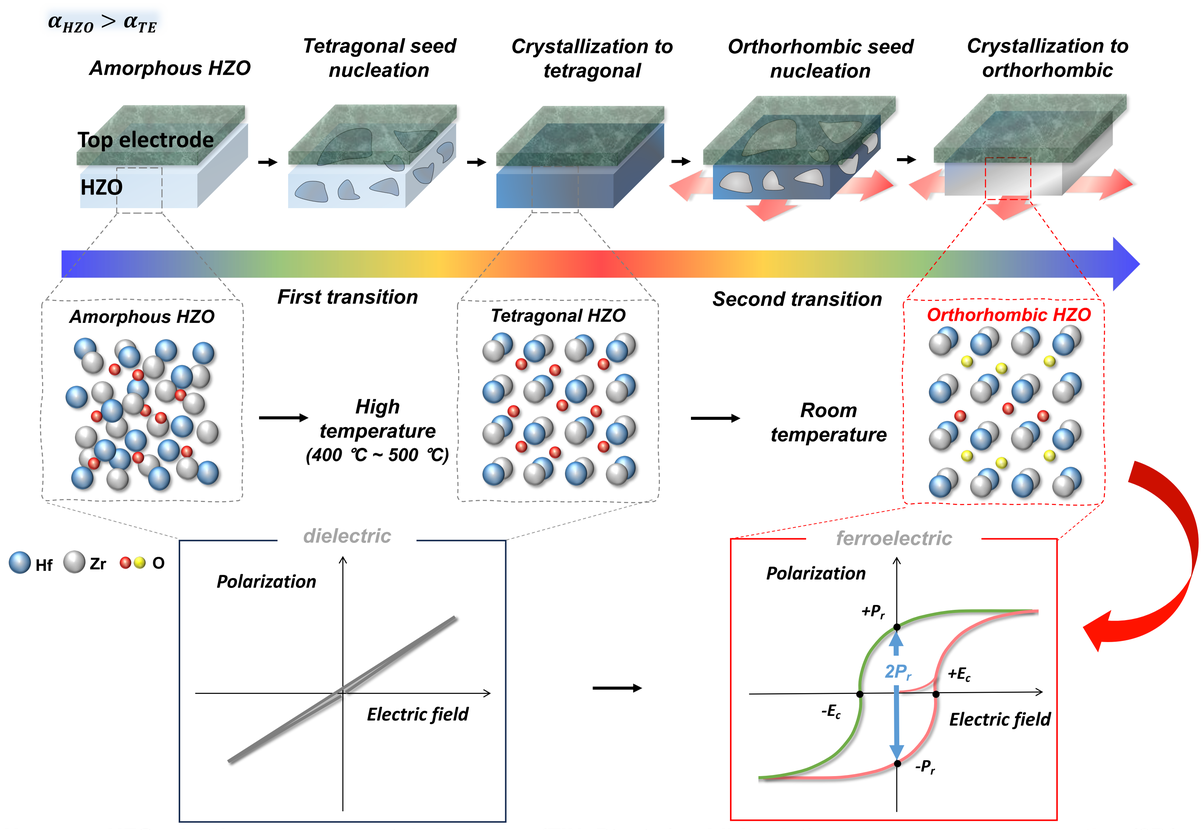
Introduction

Promising ferroelectric material : HZO

- Down-scaling capability
- CMOS compatibility
- Ferroelectricity is originated from orthorhombic phase (o-phase).

Ferroelectric o-phase stabilization mechanism : Clamping effect

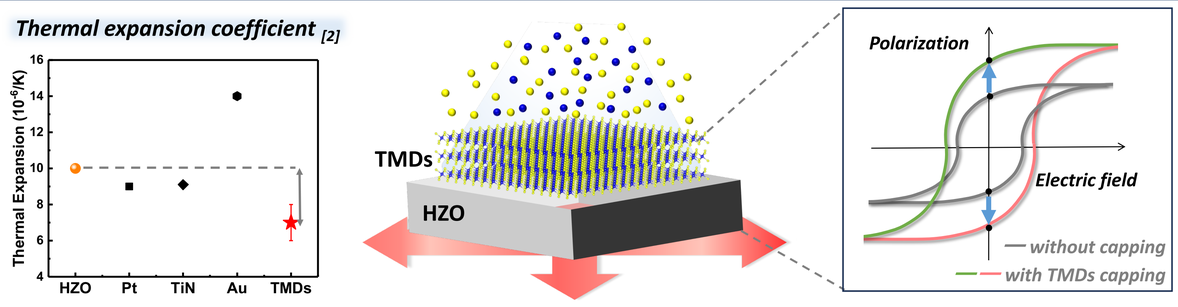
Clamping effect — O-phase is stabilized through tensile stress induced by the difference of thermal expansion coefficient of HZO and top electrode ($\alpha_{HZO} > \alpha_{TE}$) during rapid thermal annealing process.



However, HZO adapting common metal electrodes (TiN, Pt, etc.) exhibit relatively low remnant polarization ($2P_r$).

Motivation

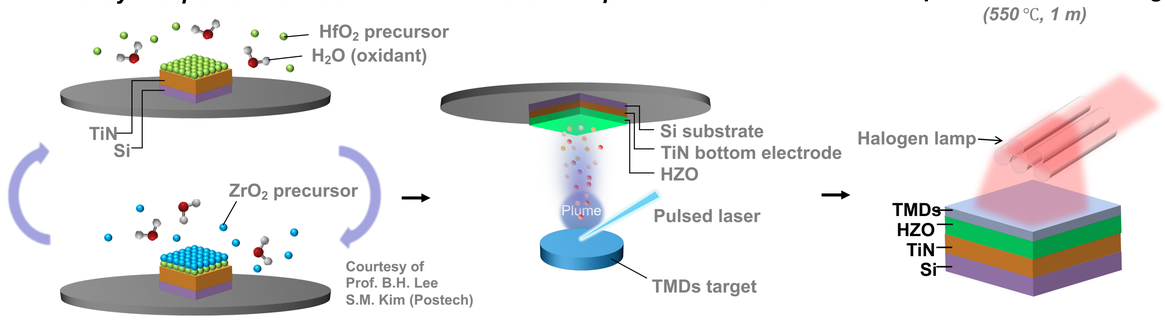
Novel capping layers : TMDs



- TMDs have larger difference of α with HZO than other electrode materials, thus they may induce larger tensile stress, o-phase fraction, and $2P_r$ value in HZO thin films.
- The larger $2P_r$, the larger memory window in FeRAM and FeFET.

Methods

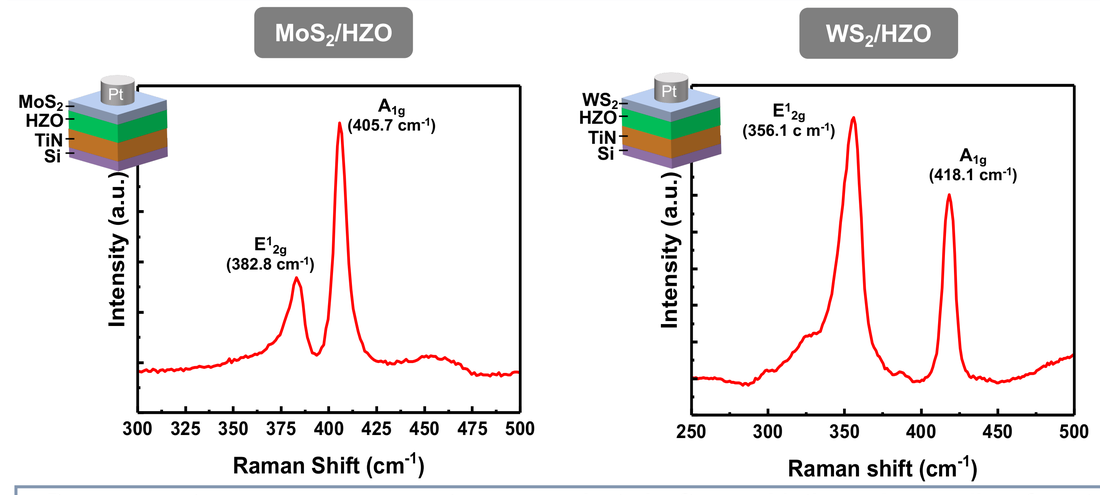
Atomic layer deposition of HZO → *Pulsed laser deposition of TMDs* → *Rapid Thermal Annealing* (550 ℃, 1 m)



- HZO (10 nm) was grown on TiN bottom electrode by atomic layer deposition, followed by TMDs growth via pulsed laser deposition with KrF (248 nm) excimer laser.
- Rapid thermal annealing was processed to induce tensile stress in HZO thin films.

Results and discussion

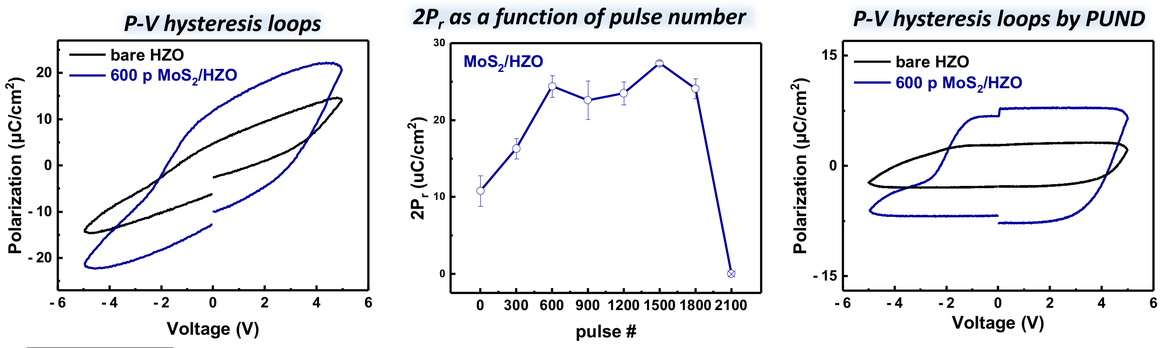
Raman Spectroscopy of TMDs/HZO



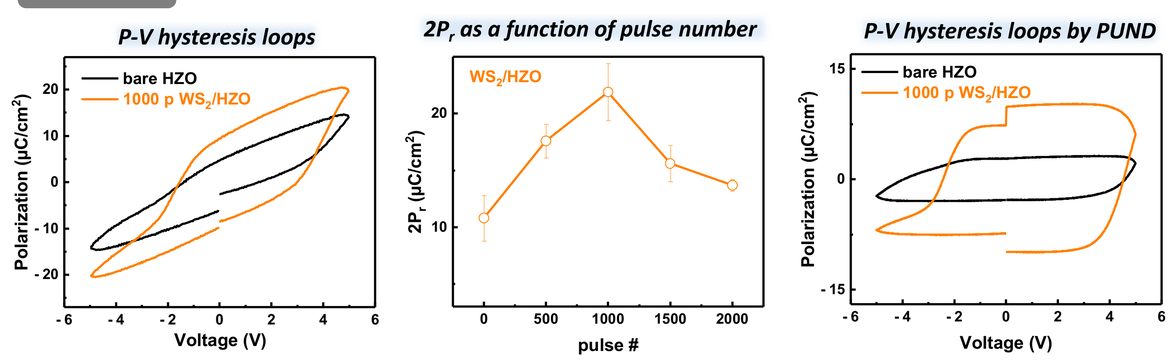
- Raman spectroscopy measurements are conducted after rapid thermal annealing for structural analysis.
- Raman spectra shows that TMDs were successfully grown by pulsed laser deposition.

Ferroelectric properties : P-V hysteresis loop

MoS_2/HZO

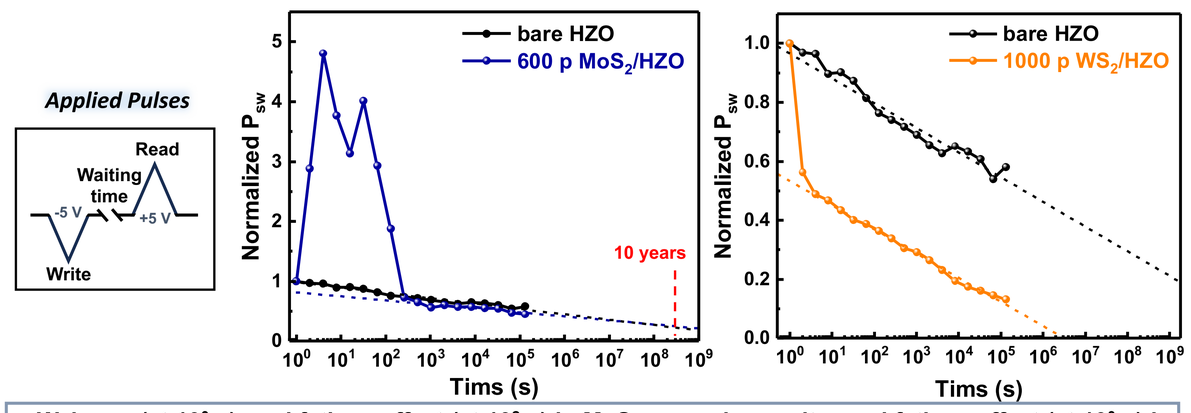


WS_2/HZO



- For MoS_2-capped HZO capacitor, $2P_r$ value is nearly saturated after 600 pulses in figure ($2P_r$ as a function of pulse number). Moreover, 1500 pulses MoS_2-capped HZO capacitor shows enhanced $2P_r$ value of 27.4 μC/cm², almost three-times higher compared to bare HZO capacitor (~10 μC/cm²).
- 1000 pulses WS_2-capped HZO capacitor shows enhanced $2P_r$ value of 21.9 μC/cm², two-times higher compared to bare HZO capacitor.
- These enhancement in $2P_r$ value can be resulted from improved o-phase fraction by introducing TMDs capping layers with lower α than HZO.
- Remarkably, $2P_r$ value enhancement is maintained when leakage current effect is excluded by PUND measurements, demonstrating ferroelectricity of TMDs-capping HZO capacitor is truly improved.

Ferroelectric properties : Retention



- Wake-up (at 10^0 s), and fatigue effect (at 10^2 s) in MoS_2-capped capacitor and fatigue effect (at 10^0 s) in WS_2-capped capacitor might be resulted from the formation of oxygen vacancies [3], due to the formation of MoO_3, WO_3, and SO_2 at the interface.
- It is observed that ferroelectric property of TMDs-capped HZO capacitor is maintained ($P_{sw} \neq 0$) more than 10^5 seconds, despite wake-up and fatigue effect in early state. Notably, polarization of 600 p MoS_2-capped capacitor is estimated to be retained more than 10 years (3 x 10^8 seconds).

Conclusion

1. The TMDs-capped HZO capacitors, fabricated by atomic layer deposition and pulsed laser deposition, exhibit two- to three-times enhanced $2P_r$ value, might be attributed to the increased o-phase fraction due to TMDs capping layer, facilitated by an enlarged clamping effect.
2. For reliability characteristics, it is confirmed that polarization of TMDs-capped HZO capacitor can endure more than 10^5 seconds, although they suffer wake-up and fatigue effect resulted from oxygen vacancies.

Reference

[1] *Adv. Mater. Interfaces* **2022**, *9*, 2102528.
[2] *Sci. Adv.* **2022**, *8*, eabo3783.
[3] *Nanoscale* **2016**, *8*, 1383.

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