Record-high *P*r (2*P*r > 40 μC/cm²) in 3 nm (Physical) Ferroelectric HZO Annealed at 450 ℃: High-T (85 ℃) Electrical Cycling and Oxygen Vacancy Engineering

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Abstract- A remarkable improvement in remnant polarization (2Pr), from below 5 μC/cm² to over 40 μC/cm², has been achieved in an ultra-thin 3 nm (physical) ferroelectric (FE) HZO layer annealed at 450 ℃, facilitated by increased oxygen vacancies (Vo/Vo²⁺) and high-temperature electrical cycling (HTEC) at 85 ℃. Notably, this enhancement persists upon returning to room temperature (RT). Systematic characterization attributes the record-high 2*P*r in the 3 nm HZO layer to a Vo/Vo²⁺-assisted phase transition from initially dominant tetragonal (t)-phase to FE orthorhombic (o)-phase. First-principles calculations reveal that the increased Vo²⁺ during HTEC is crucial for driving the t-to-o phase transition, shifting the free energies of the t- and o-phases, and ultimately stabilizing the o-phase over the t-phase. Our work unlocks new opportunities for optimizing ultra-thin FE layers with a low thermal budget, laying the foundation for the next-generation of FE memory devices.

I. Introduction

The thickness down-scaling of HfO_2-based FE films has sparked growing interest from both academia and industry [1-2], driven by the demand for high-density and ultra-low-power FeRAMs. However, as the film thickness decreases, the FE o-phase in polycrystalline films diminishes, while more stable t-phase dominates [3-5], leading to a significant degradation in FE performance [Fig. 1(a)]. To address this challenge, various approaches have been explored to transit the majority t-phase to the o-phase [5-8]. However, these phase-transition attempts still face several limitations, including (1) a high thermal budget (>500 ℃) [5][9], which restricts their compatibility with BEOL processes, and (2) only marginal improvements, especially for ultra-thin 3 nm HZO layers, where 2*P*r remains below 10 μC/cm²[5].

In this work, we propose and experimentally demonstrate an effective Vo²⁺-assisted t-to-o phase transition in an ultra-thin 3 nm HZO layer annealed at BEOL-compatible temp. of 450 ℃. First-principles calculations are performed to unveil the mechanisms driving this transition. In ultra-thin HZO layers, the t-phase is initially more stable due to its lower free energy compared to the o-phase. However, as Vo²⁺ concentration increases beyond a critical threshold, the free energy difference between the t-phase and o-phase gradually diminishes, and eventually reverses, stabilizing o-phase over the t-phase. Key achievements of this work are summarized in Fig. 1(b).

II. Characterization and Analysis of Ferroelectricity

A. Challenges of degraded ferroelectricity in ultra-thin HZO

The thickness of our thin HZO films is precisely controlled via atomic-layer-deposition (ALD) at 300 ℃, with TEMAHf, TEMAZr and ozone as the precursors. The *PV* loops of 3/4/5 nm HZO capacitors annealed at 450°C are shown in Fig. 2(a), indicating a rapid decline in 2*P*r as thinning HZO. Although a higher anneal temp. of 550°C effectively enhances 2*P*r [Fig. 2(b)], further improvements are still desired under lower thermal budgets for potential BEOL applications. However, the conventional wake-up cycling at RT achieves only limited enhancement in ferroelectricity for the HZO annealed at 450°C [Fig.2(c)], with the final 2*P*r still constrained to around 6 μC/cm² [Fig.2(d)].

B. Discovery of remarkable ferroelectricity enhancement and increased Vo/Vo²⁺ under HTEC in 3 nm HZO layer

To further enhance *P*r in ultra-thin HZO annealed at 450°C, we employ HTEC, inspired by its wake-up effect previously observed in 10 nm thick HZO layers [10]. The HTEC process and waveforms are illustrated in Fig. 3(a)-(b).

GIXRD analysis in Fig. 3(c), along with the initial anti-FE (AFE) *PV* loop in Fig. 2(c), confirms the dominance of the t-phase in the 3 nm HZO annealed at 450°C. Notably, the initial AFE-like *PV* and *IV* loops gradually transform into FE-like loops during HTEC, indicating a potential phase transition from t-phase to o-phase [Fig. 3(d)], which will be further confirmed later. As a result, the 2*P*r is significantly enhanced from less than 5 μC/cm² to around 20 μC/cm², and this improvement persists even upon returning to RT [Fig. 4(a-c)].

Meanwhile, a significantly more pronounced increase in leakage current is observed compared to RT cycling [Fig.4 (d)], suggesting a promoted augmentation and redistribution of Vo/Vo²⁺ during the HT process [Fig. 4(e)]. This increased concentration is further confirmed by EELS spectra showing the *O-K* ionization edge of HZO before and after HTEC [Fig. 5(a)]. The increased ratio of peak B to peak A implies more Vo/Vo²⁺ generation [Fig. 5(b)] [11]. These results suggest a potential correlation between the enhanced ferroelectricity and the increased Vo/Vo²⁺ concentration.

C. Further boosting 2*P*r through enhanced Vo/Vo²⁺-assisted t-to-o phase transition

To further verify the role of Vo/Vo²⁺ in enhancing 2*P*r, another 3 nm HZO film with an initially higher Vo/Vo²⁺ concentration [Fig. 5(c)], tuned during ALD deposition, was fabricated and characterized. The initial 2*P*r [Fig. 5(d)] is increased, and an enhanced 2*P*r after wake-up at RT is achieved [Fig. 5(e)], illustrating that higher Vo/Vo²⁺ concentrations promote o-phase formation. Moreover, 2*P*r enhancement becomes more pronounced during HTEC, with all *PV*, *IV*, and *CV* loops in Fig 6(a) further corroborating the t-to-o phase transition. This enhancement remains stable upon returning to RT, as shown in Figs. 6(b-c).

The dielectric constants (*k*) of the 3 nm FE layer during HTEC are extracted from *CV* [Fig 6(a)] and summarized in Fig. 7(a). The notable continuous decrease in *k* convincingly confirms that the enhancement in ferroelectricity of our 3 nm HZO can be primarily attributed to the t-to-o phase transition rather than to other potential competing factors, which exhibit different trends in *k* changes [12-13]. Furthermore, the HAADF imaging after HTEC directly visualizes the presence of o-phase at the atomic level [Fig. 7(b-d)].

Driven by the enhanced Vo/Vo²⁺-assisted t-to-o phase transition, our 3 nm HZO annealed at 450 ℃ exhibits exceptional performance, achieving 2*P*r exceeding 40 μC/cm² at 1V and over 15 μC/cm² at 0.6 V [Fig. 8(a)] with good uniformity [Fig. 8(b)]. Robust retention and endurance characteristics are shown in Fig. 8 (c)-(e).

Additionally, the improvement in the 3 nm HZO film annealed at 550℃, with a larger portion of o/t-phases [Fig. 9(a)], is also investigated. The limited improvement in 2*P*r after HTEC [Fig. 9(b)] and the slight reduction in *k* [Fig. 9(c)] suggest a restricted t-to-o phase transition. This anneal temp. dependent improvement [Fig. 9(d)] is attributed to the varying initial proportions of t-phase, which transition to the o-phase during HTEC [Fig. 9(e)].

III. Unveiling the Critical Role of Vo/Vo²⁺

Experimental results suggest that Vo/Vo²⁺ promote the t-to-o phase transition. To differentiate the effects of Vo and Vo²⁺, first-principles calculations were performed on HZO supercell with varying Vo or Vo²⁺ concentrations (Fig. 10).

Phase transitions are governed by the thermodynamic driving force, defined as the free-energy difference between the initial and final phases, and the kinetic activation energy. In ultra-thin HZO films, smaller grain sizes increase the t-to-o phase kinetic barrier and decrease the free-energy of t-phase, making the t-phase more stable than the o-phase [Fig.11(a)]. Calculation results in Fig.11(b) reveal that increased Vo²⁺ favors o-phase stability, whereas Vo has the opposite effect. This is consistent with the enhanced 2*P*r observed during HTEC, which is more effective at generating Vo²⁺ [Fig.11(c)]. The agreement between experiment and simulation strongly supports Vo²⁺-assisted 2*P*r enhancement in ultra-thin HZO film by stabilizing o-phase than t-phase and promoting the t-to-o phase transition. Based on these findings, a design guideline for optimizing FE properties in ultra-thin HZO film by Vo² engineering is proposed [Fig.11(d)].

IV. Conclusion

At a low anneal temp. of 450°C, the t-phase initially exhibits greater stability than the o-phase in ultra-thin FE layers. However, the increase in Vo²⁺ concentration reverses this stability trend [Fig. 12(a)], offering a new pathway to significantly enhance 2*P*r [Fig. 12(b)]. Through comprehensive characterization and simulations, we unveil and harness this phenomenon to achieve an effective t-to-o phase transition in BEOL-compatible ultra-thin 3 nm HZO layers, resulting in a remarkable 40 μC/cm² boost in 2*P*r [Fig. 12(c)]. This work provides critical insights into unleashing the full potential of ultra-thin FE layers, driving advances in future high-performance, low-power applications.

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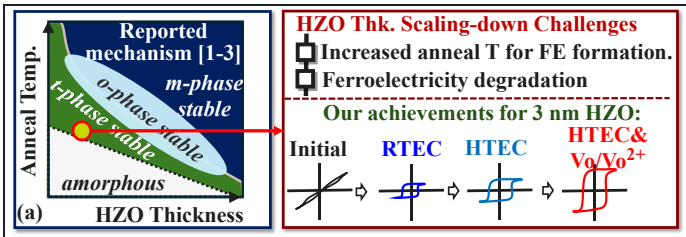
Reference [1] M. Lee *et al.*, VLSI 2024. [2] N. Ramaswamy *et al.*, IEDM 2023.[3] K. Tahara *et al.*, VLSI 2021[4] J. Wu *et al.*, APL 2020[5] D. Zhang *et al.*, VLSI 2024.[6] Z. Gao *et al.* EDL 2021.[7] C. Wang *et al.* JMCC 2021.[8] X. Tian *et al.* APL 2018.[9] S. Kim *et al.*, EDL 2021. [10] Z. Zhang *et al.*, APL 2023.[11] S.Ostanin *et al.*, PRB 2000.[12] C. Cho *et al.*, IEDM 2023.[13] M. Pešić *et al.*, AFM 2016. [14] M.I. Popovici *et al.*, IEDM 2022.



(b)

Highlights

I.Achievement of a record-high *Pr* (>40 μC/cm²) in ≤ 3 nm (physical) HZO with a low thermal budget of 450 °C.

II.Identification of the t→o phase transition as the main contributor to *Pr* enhancement.

III. The phase change is unveiled to be driven by the enhanced stability of o-phase over t-phase, achieved through increased Vo^{2+}.

	VLSI[5]	EDL[6]	JMCC[7]	APL[8]	Ours
FE Thk. (nm)	3	1.5	3	3	3
2*Pr* (μC/cm²)	<10	<4	~16	~5	>40
Anneal *T*(°C)	500	700	450	650	450

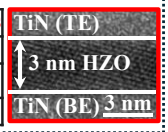


Fig.1 (a) Our findings address the degraded FE properties and high anneal temp. challenges. (b) Highlights of this work, including benchmarking with physical 3 nm and sub-3 nm FE layers, and TEM image.

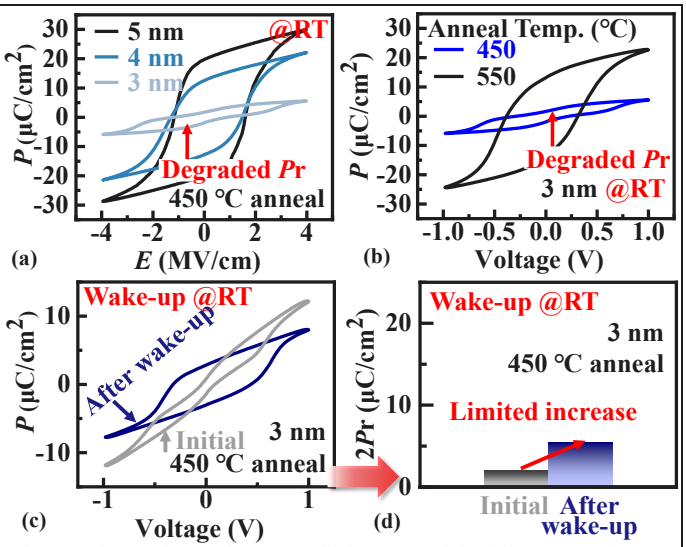
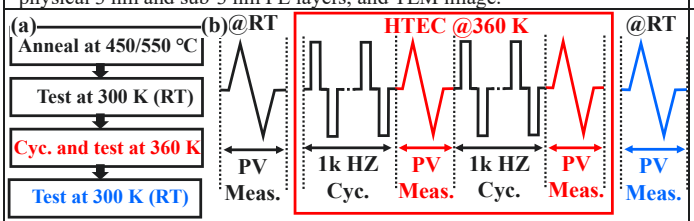
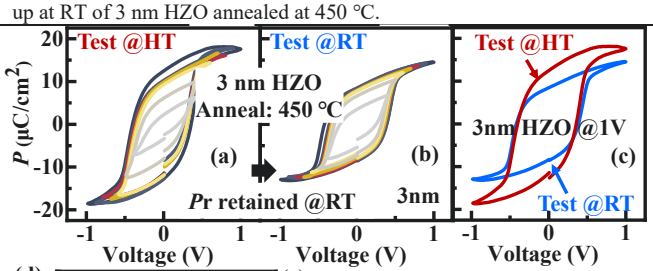


Fig.2. PV loops of (a) various HZO thicknesses and (b) different anneal temp. of 3 nm HZO. *Pr* degrades with thinning HZO thickness and lower anneal temp. (c) Wake-up effect at RT in 3 nm HZO. (d) Limited increase after wake-up at RT of 3 nm HZO annealed at 450 °C.





HTEC (85°C): 3 nm HZO annealed at 450 °C

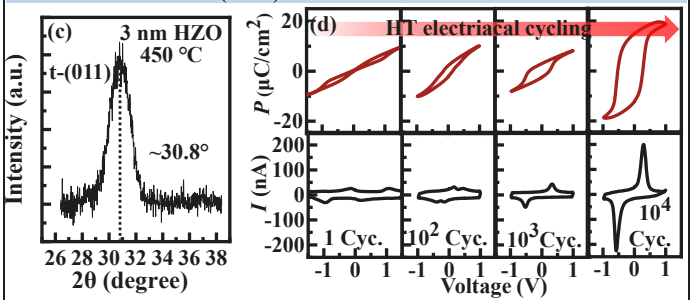


Fig.3. (a) HTEC process flow and (b) waveforms. (c) GIXRD of 3 nm HZO annealed at 450 °C with a peak near 30.8° indicative of t-phase. (d) Evolution of *PV* and *IV* loops during HTEC, transforming from AFE-like to FE-like loops, suggesting a potential t-to-o phase transition.

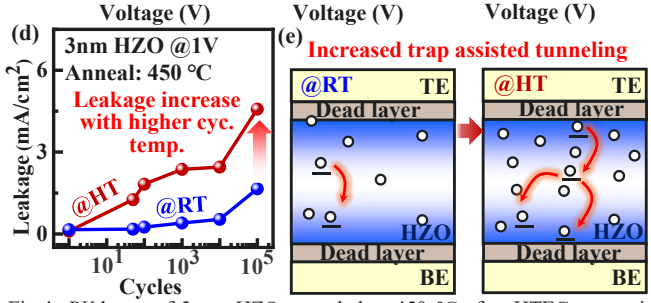


Fig.4. *PV* loops of 3 nm HZO annealed at 450 °C after HTEC at varying applied voltages tested at (a) HT and (b) RT. (c) Enhanced ferroelectricity can be well retained even after returning to RT. (d) Increased leakage currents after HTEC, likely induced by (e) augmentation and redistribution of Vo^{2+} during HTEC.

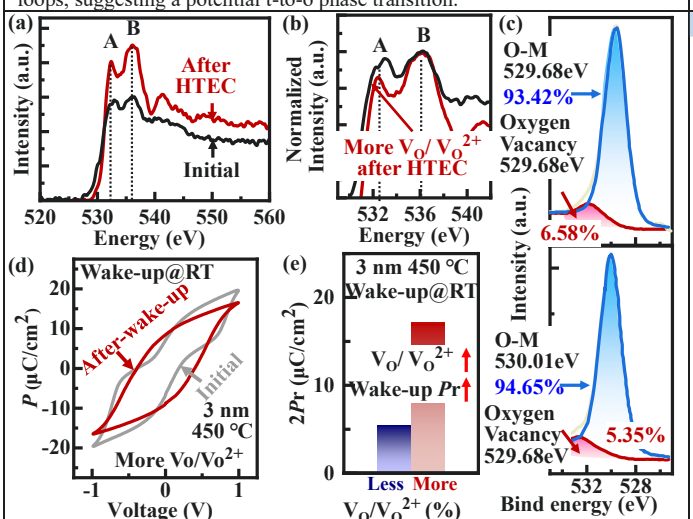


Fig. 5. (a) EELS spectra of the 3 nm HZO layer before and after HP cycling. (b) Doublet peaks (A and B) with normalized maximum intensity of peak B, indicating increased Vo/Vo^{2+} after HTEC. (c) XPS of HZO films with different initial Vo/Vo^{2+} levels. (d) Wake-up *PV* loops of 3 nm HZO with more Vo/Vo^{2+}, realizing (e) enhanced 2*Pr* improvement.

HTEC(85°C): 3 nm HZO (more Vo/ Vo^{2+}) annealed at 450 °C

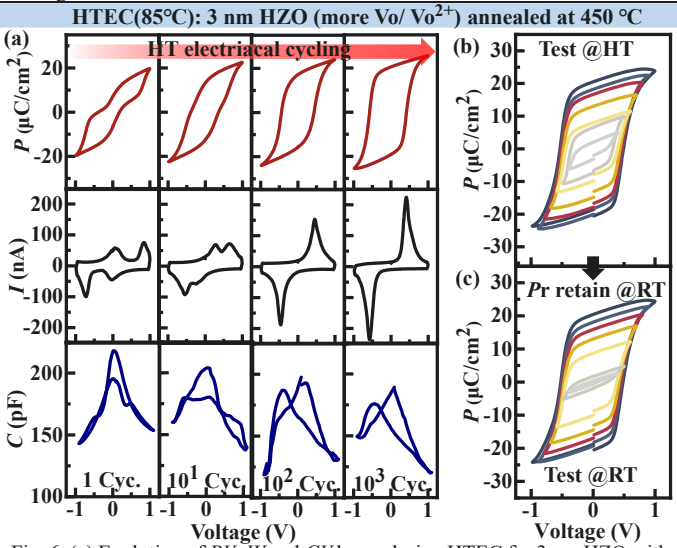


Fig. 6. (a) Evolution of *PV*, *IV* and *CV* loops during HTEC for 3 nm HZO with more Vo/Vo^{2+} annealed at 450 °C, suggesting the potential t-to-o phase transition. (b) *PV* loops after HTEC, achieving 2*Pr*>40 μC/cm² at 1 V, which are (c) well retained upon returning to RT.

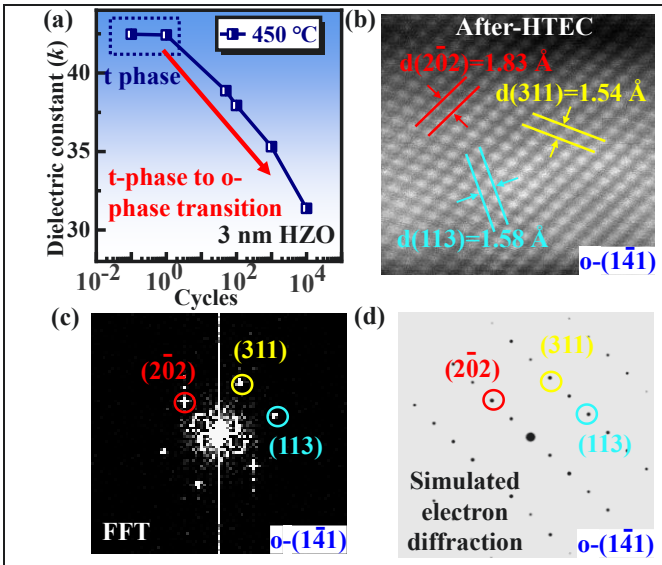


Fig.7. (a) Continuous decrease in k during HT cycling confirms the t-to-o phase transition. (b) HAADF further visualizes the presence of o-phase, with good consistence between (c) FFT results and (b) Simulated ED.

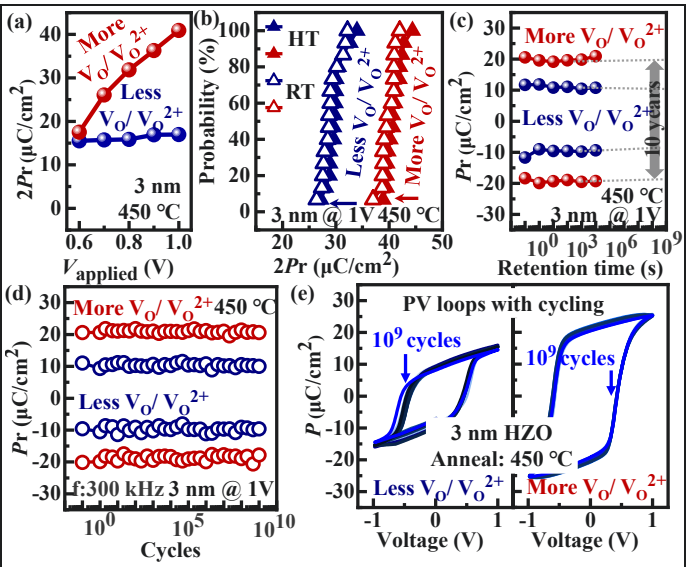


Fig. 8. Outstanding performance of 3 nm HZO layers after t-to-o phase transition: (a) low-voltage applicability, (b) good uniformity, (c) stable retention. (d) robust endurance>10^9 cycles with (e) consistent PV loops.

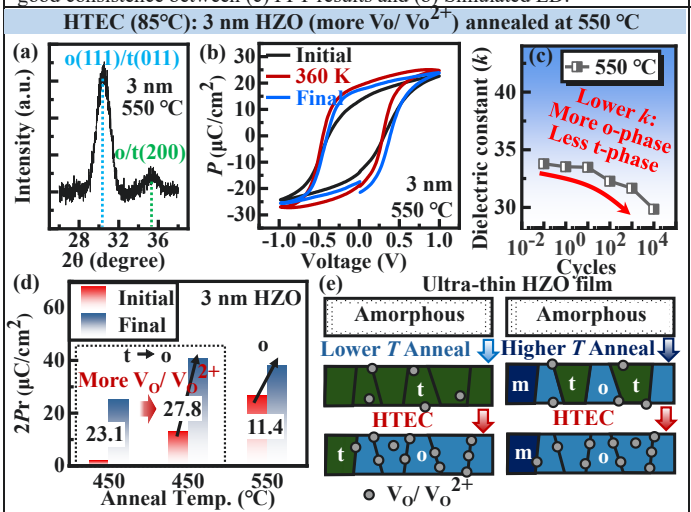
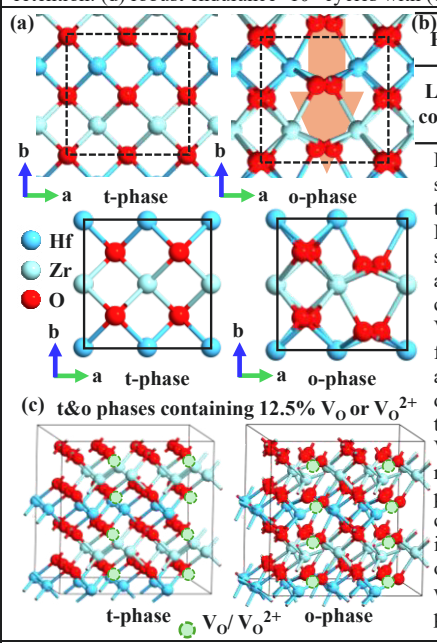


Fig. 9. (a) GIXRD of 3 nm HZO annealed at 550 °C, revealing a higher proportion of o/t phases. (b) The minimal $2Pr$ improvement after HTEC and (c) a slight decrease in k indicate a limited t-to-o phase transition. (d) Anneal temp.-dependent $2Pr$ improvements are attributed to (e) initially different proportion of formed t-phase which transitions to o-phase during HTEC.



(b)

Phase	t-phase ($P4_2/nmc$)	o-phase ($Pca2_1$)
Lattice constant	a=5.11 Å c=5.25 Å	a=5.08 Å b=5.11 Å c=5.30 Å

Fig.10. (a) Atomic structure of the unit cell for the t-phase and o-phase. (b) Lattice constant and (c) schematics of the t-phase and o-phase supercells containing 12.5% Vo or Vo^{2+}. Comprehensive first-principles calculations are conducted to distinguish and quantify the contributions of Vo and Vo^{2+} to the changes in the relative stability of the t-phase and o-phase. These calculations offer insights into the Pr enhancement observed in our 3 nm HZO with initially dominant t-phase during HPEC.

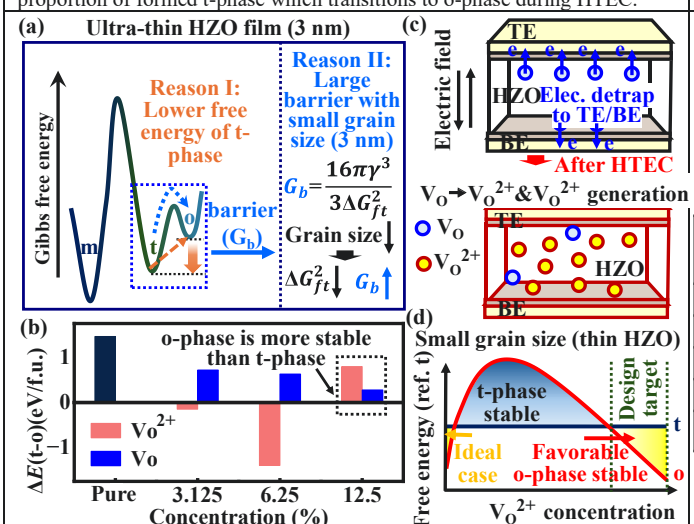
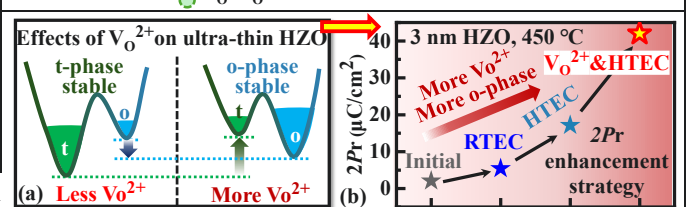


Fig.11. (a) The t-phase dominates in ultra-thin HZO films. (b) Calculation results reveal that increasing Vo^{2+} beyond a critical threshold stabilizes the o-phase over the t-phase, consistent with the t-to-o phase transition observed in HTEC, (c) which significantly increases Vo^{2+} generation. (d) Guided by these results, the design target to favor the o-phase in ultra-thin HZO is proposed.



(c)	Thk. (nm)	Anneal T (°C)	Phase trans.	$2Pr$ (μC/cm^2) Initial	$2Pr$ (μC/cm^2) Final	Analysis k	XRD	HAADF	DFT
[5]	3	500	t→o	~4	~8	✖	✖	✖	✓
[9]	6	500	t→o	1	5	✓	✖	✓	✖
[12]	4	NA	t→o	1	28	✓	✖	✖	✖
[14]	6.5	550	t→o	28	66.5	✖	✓	✖	✖
This work	3	450	t→o	<5	>40	✓	✓	✓	✓

Fig.12 (a) Unveiled effects of increased Vo^{2+} on stabilizing the o-phase over the t-phase in the ultra-thin FE layer, facilitating t-to-o phase transition. Building on these findings, (b) new insights and strategies are developed to enhance $2Pr$ in ultra-thin FE layers at low anneal temp., resulting in a ~40 μC/cm^2 boost in $2Pr$ for the 3 nm HZO layer. (c) A benchmark table compares reported efforts to utilize t-to-o phase transition, with our work effectively extending the feasibility to BEOL-compatible 3 nm HZO layer.