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Interface engineering of HfO₂-based ferroelectric devices for crystal phase control and enhanced ferroelectricity using atomic-layer-deposited ZrO₂ nucleation layers

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Interface engineering is a key for high-performance HfO₂-based ferroelectric devices. In this study, the fabrication techniques for HfO₂-based thin films using atomic-layer-deposited ZrO₂ nucleation layers [atomic layer deposition (ALD)-ZrO₂-NLS], which are inserted at ferroelectric/electrode interfaces, are systematically summarized. ALD-ZrO₂-NLS were found to promote crystallization and formation of the ferroelectric orthorhombic (O) phase in HfO₂-based films, resulting in superior ferroelectricity. This is attributed to two critical roles of ALD-ZrO₂-NLS: providing a seed layer that induces epitaxial-like grain growth because of the high degree of lattice matching between the pre-crystallized ALD-ZrO₂-NL and the O phase of HfO₂, and acting as a stressor layer that induces tensile stress due to the difference in thermal expansion coefficients during annealing process. In addition, improved reliability and a low-temperature fabrication process for HfO₂-based thin films are demonstrated using ALD-ZrO₂-NLS. These findings suggest that interface engineering using ALD-ZrO₂-NLS is a promising approach for fabricating next-generation HfO₂-based ferroelectric devices. © 2026 The Author(s). Published on behalf of The Japan Society of Applied Physics by IOP Publishing Ltd

1. Introduction

Doped HfO₂ thin films were reported to show ferroelectricity in 2011, and ferroelectric HfO₂-based thin films have since attracted significant attention for use in future non-volatile memory device applications.^{1,2} HfO₂-based materials are compatible with complementary metal-oxide-semiconductor (CMOS) technology because they have already been well-established as gate dielectrics in conventional CMOS devices.³ In addition, HfO₂-based thin films can be deposited by atomic layer deposition (ALD), which is a requirement for films to be conformally deposited on complex three-dimensional structures of cutting-edge semiconductor devices.⁴ HfO₂-based materials also exhibit a unique advantage in thickness scalability, maintaining robust ferroelectricity even when their film thickness is less than 10 nm.⁵ Such scalability remains a significant challenge for conventional perovskite ferroelectric materials such as Pb(Zr_xTi_{1-x})O₃ because of their severe size effect.^{6,7} In addition, HfO₂-based thin films with robust ferroelectricity can be achieved even at a low process temperature of less than 400 °C, which is compatible with the thermal budget requirements of back-end-of-line (BEOL) processes.^{8–11} Therefore, ferroelectric HfO₂-based materials are considered promising candidates for use in future ferroelectric devices with higher performance and lower power consumption, such as ferroelectric random access memory, ferroelectric field-effect transistors (FeFETs), and ferroelectric tunnel junctions.^{6,12,13}

The origin of ferroelectricity in HfO₂-based materials is thought to be displacement of oxygen atoms in a unit cell of the non-centrosymmetric orthorhombic (O) phase with space group *Pca*2₁.¹⁴ Thus, to achieve superior ferroelectricity, crystallization of a HfO₂-based thin film and an increase in the ratio of the ferroelectric O phase to the non-ferroelectric phases in the film are required. However, numerous researchers have reported that the fraction of the O phase in

HfO₂-based thin films is affected by numerous factors, including dopants, electrodes, thickness, and annealing conditions, because this phase is metastable, whereas the stable phase is a paraelectric monoclinic (M) phase.^{13,15–17} Therefore, the selection of those conditions is critical for determining the crystal structure of HfO₂-based thin films.

TiN is typically used as an electrode material to fabricate HfO₂-based metal–ferroelectric–metal (MFM) capacitors because TiN electrodes provide mechanical tensile stress due to the difference in thermal expansion coefficients between TiN ($9.4 \times 10^{-6} \text{ K}^{-1}$) and HfO₂ ($6.5 \times 10^{-6} \text{ K}^{-1}$); TiN electrodes also induce oxygen vacancies (V_O) in HfO₂-based thin films because of the scavenging effect of TiN during the annealing process, promoting the formation of the O phase.^{18–22} HfO₂-based thin films have been reported to exhibit a high remanent polarization ($2P_r = P_r^+ - P_r^-$) of $48 \mu\text{C cm}^{-2}$ even after an annealing process at a low temperature of 400 °C when a HfO₂-based thin film was sandwiched with TiN top and bottom electrodes (TE- and BE-TiN) for the fabrication of MFM capacitors.^{18,23} Many other electrode materials, including Si,^{9,20,24} TaN,²⁵ Ir,²⁶ Pt,²⁷ W,¹⁹ and RuO₂,²⁸ have been used for HfO₂-based MFM capacitors; however, the crystallinity and ferroelectricity of the HfO₂-based thin films were found to be strongly dependent on the choice of electrode material. Considering practical applications of ferroelectric devices composed of various electrode materials, engineering of the interface between the ferroelectric HfO₂-based thin film and the electrode is required to achieve superior ferroelectricity irrespective of the electrode materials.

HfO₂-based thin films generally show fatigue phenomena (i.e. degradation of their $2P_r$ values with increasing number of switching cycles).^{29,30} This unstable switching behavior depending on the number of switching cycles is a major reliability issue that needs to be overcome for HfO₂-based thin films to be used in practical applications. The origin of fatigue has been attributed to pinning of domains caused by V_O formed during



field cycling.²⁹⁾ In addition, Onaya et al. reported that additional V_O should be formed in HfO_2 -based films because of the interfacial reaction induced by electric field cycling between a HfO_2 -based film and a TiN electrode.^{31–33)} To overcome these reliability issues, the precise design of the interface between a HfO_2 -based film and electrodes is necessary.

Various interfacial layers (ILs) inserted between ferroelectric HfO_2 -based films and electrodes have been reported to improve the ferroelectricity (Table I).^{9,34–62)} For the Al_2O_3 -IL case, the ferroelectricity of HfO_2 -based thin films has been reported to be enhanced through optimization of the thickness and the insertion position.^{36,46,49–51)} In addition, the leakage current for the overall films was reduced when an Al_2O_3 -IL was used because of its amorphous structure and larger bandgap (~ 8.8 eV) compared with that for HfO_2 (~ 5.8 eV).^{63–65)} However, increasing the total capacitance equivalent thickness (CET) has raised concerns because the dielectric constant (k) for Al_2O_3 ($k \approx 9$) is lower than that for ferroelectric HfO_2 ($20 \leq k \leq 40$).^{63,64,66,67)} In addition, because most of the applied voltage drop occurs across the Al_2O_3 -IL, which has a lower k value, the Al_2O_3 -IL can prevent HfO_2 -based thin films from fully exhibiting their ferroelectricity.³⁴⁾ Consequently, a thicker Al_2O_3 -IL cannot be used without sacrificing device performance. Previous studies have also shown that a TiO_2 -IL promotes the formation of the ferroelectric O phase, driven by the difference in thermal expansion coefficient between TiO_2 ($5 \times 10^{-5} \text{ K}^{-1}$) and HfO_2 ($6.5 \times 10^{-6} \text{ K}^{-1}$).^{41,68)} Although TiO_2 has the advantage of a higher k value ($40 \leq k \leq 110$) than that for ferroelectric HfO_2 ($20 \leq k \leq 40$), its smaller bandgap (~ 3.5 eV) may cause increased leakage current.^{63,64,66,69–71)} HfO_2 itself has also been investigated as an IL to enhance the ferroelectricity of HfO_2 -based thin films.^{41,43,56–58)} Onaya et al. reported that HfO_2 -based thin films stacked with a HfO_2 -IL predominantly formed the stable M phase after an annealing process.³⁹⁾ This behavior is attributed to the crystal structure of HfO_2 -based thin films being stabilized by the HfO_2 -IL with a large M-phase fraction because HfO_2 forms the stable M phase preferentially over the metastable O phase. Therefore, precise optimization of film thickness and annealing conditions is required when using HfO_2 -ILs. On the other hand, Onaya et al. were the first to report that using an ALD- ZrO_2 -IL as a nucleation layer (NL) to promote

crystallization and O-phase formation resulted in enhanced ferroelectricity,^{9,34,35)} the details of these studies will be discussed later. Numerous authors have also reported that superior ferroelectricity can be attained using a ZrO_2 -IL.^{36,37,40–47)} The physical properties of ZrO_2 (e.g. k value, bandgap, and lattice parameters) are similar to those of HfO_2 , which is expected to lead to high material compatibility within devices employing an ALD- ZrO_2 -IL.

In this paper, we comprehensively review interface engineering using ALD- ZrO_2 -NLs to achieve crystal phase control and superior ferroelectricity in HfO_2 -based thin films. This paper discusses the effect of ALD- ZrO_2 -NLs and their insertion position by comparison with other types of ILs. The improved reliability of HfO_2 -based thin films fabricated using ALD- ZrO_2 -NLs is also discussed. Furthermore, the low-temperature fabrication of a HfO_2 -based metal–ferroelectric–semiconductor (MFS) structure, which is a basic structure of FeFETs, is demonstrated at 300°C using ALD- ZrO_2 -NLs. This review focuses on studies in which $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ (HZO) thin films were mainly used as ferroelectric films because, compared with the other HfO_2 -based thin films with various dopants, they provide stable ferroelectricity even with a low thermal budget ($< 400^\circ\text{C}$)^{8–11)} and even over a wide composition range centered on a Hf/Zr ratio of 1:1.^{25,66,72)} In addition, we employed a unique ALD approach for HZO films using a $(\text{Hf/Zr})[\text{N}(\text{C}_2\text{H}_5)\text{CH}_3]_4$ (Hf:Zr = 1:1) cocktail precursor, in which $\text{Hf}[\text{N}(\text{C}_2\text{H}_5)\text{CH}_3]_4$ and $\text{Zr}[\text{N}(\text{C}_2\text{H}_5)\text{CH}_3]_4$ precursors are pre-mixed in a ratio of 1:1.^{10,11,34,35)}

2. Crystal phase control using ALD- ZrO_2 -NLs

2.1. Role of ALD- ZrO_2 -NLs in crystal phase control

First, we investigated NLs to promote the formation of the ferroelectric O phase and enhance the ferroelectricity in HZO thin films. The crystallization onset temperature for ZrO_2 is known to be lower than that for HfO_2 . One of our previous studies also revealed that a ZrO_2 film deposited by ALD at 300°C using $(\text{C}_5\text{H}_5)\text{Zr}[\text{N}(\text{CH}_3)_2]_3$ as a precursor formed a polycrystalline structure consisting predominantly of O, tetragonal (T), and cubic (C) phases even after the ALD process, whereas an ALD-HZO film formed an amorphous structure, as determined by X-ray diffraction (XRD) analysis (Fig. 1(a)).³⁴⁾ In addition, the as-grown ALD- ZrO_2 film with

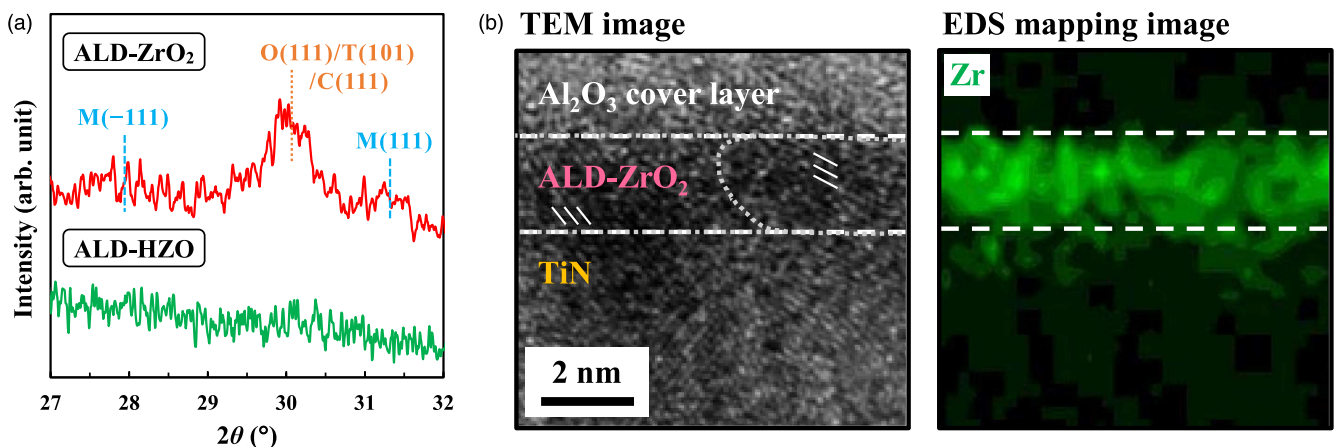


Fig. 1. (a) XRD patterns for as-grown ZrO_2 and HZO films deposited by ALD at 300°C . (b) Cross-sectional TEM and EDS mapping images of as-grown ALD- ZrO_2 film with thickness of 2 nm deposited on TiN substrate. Reproduced from Ref. 34 with permission of IOP Publishing. Copyright 2017 The Japan Society of Applied Physics.

Table I. Various ILs for interface engineering between HfO₂-based thin film and electrodes.^{9,34–58)}

IL		HfO ₂ -based film		Annealing			TE/BE material	Device type	Year	References
Material	Thickness	Material	Thickness	Temperature	Annealing type					
ZrO ₂	0.5–5 nm	HZO	10 nm	600 °C	PDA	TiN/TiN	MFM	2017	Onaya et al. ³⁴⁾	
	2 nm	HZO	10–25 nm	400 °C–700 °C	PDA	TiN/TiN	MFM	2019	Onaya et al. ³⁵⁾	
	2 nm	HZO	9.5 nm	900 °C	PMA	TiN/Si	MFS	2019	Lee et al. ³⁶⁾	
	1.5 nm	HZO	12 nm	550 °C	PMA	TaN/Si	MFS	2019	Xiao et al. ³⁷⁾	
	10 nm	HZO	10–30 nm	600 °C	PDA	TiN/TiN	MFM	2020	Onaya et al. ³⁸⁾	
	10 nm	HZO	10 nm	600 °C	PDA	TiN/TiN	MFM	2020	Onaya et al. ³⁹⁾	
	2 nm	HZO	10 nm	500 °C–800 °C	PMA	TiN/TiN	MFM	2020	Lee et al. ⁴⁰⁾	
	1 nm	HZO	10 nm	300 °C–400 °C	PMA	TiN/TiN	MFM	2021	Gaddam et al. ⁴¹⁾	
	1 or 2 nm	La-doped HZO	10 nm	550 °C	PMA	TiN/TiN	MFM	2021	Popovici et al. ⁴²⁾	
	2 or 10 nm	HZO	10 nm	300 °C	PMA	TiN/Si	MFS	2022	Onaya et al. ⁹⁾	
	1 nm	HZO	4.5 or 9.5 nm	300 °C–500 °C	PMA	TiN/TiN	MFM	2023	Yu et al. ⁴³⁾	
	1 nm	HZO	13 nm	450 °C–650 °C	PDA	TiN/TiN	MFM	2023	Song et al. ⁴⁴⁾	
	1–2 nm	HZO	12 nm	350 °C	PDA	Au/Ti/TiN	MFM	2023	Liu et al. ⁴⁵⁾	
	1 nm	HZO	10 nm	450 °C	PMA	TiN/TiN	MFM	2024	Li et al. ⁴⁶⁾	
	2 nm	HZO	8 nm	450 °C–600 °C	PMA	TiN/TiN	MFM	2024	Yang et al. ⁴⁷⁾	
Al ₂ O ₃	2 nm	HZO	10 nm	600 °C	PDA	TiN/TiN	MFM	2017	Onaya et al. ³⁴⁾	
	2 nm	HZO	9.5 nm	900 °C	PMA	TiN/Si	MFS	2019	Lee et al. ³⁶⁾	
	4–20 nm	HZO	20 nm	500 °C	PMA	TiN/TiN	MFM	2019	Si et al. ⁴⁸⁾	
	0.8–3.2 nm	HZO	21.6 nm	450 °C	PMA	TiN/TiN	MFM	2021	Chen et al. ⁴⁹⁾	
	1 nm	HZO	10 nm	550 °C	PDA	TiN/W or TiN/TiN	MFM	2021	Liu et al. ⁵⁰⁾	
	1 nm	HZO	4.5 or 9.5 nm	300 °C–500 °C	PMA	TiN/TiN	MFM	2023	Yu et al. ⁴³⁾	
	1 nm	HZO	10 nm	800 °C	Unknown	TiN/TiN	MFM	2023	Hsain et al. ⁵¹⁾	
	1 nm	HZO	10 nm	450 °C	PMA	TiN/TiN	MFM	2024	Li et al. ⁴⁶⁾	
	1 nm	HZO	10 nm	300 °C–400 °C	PMA	TiN/TiN	MFM	2021	Gaddam et al. ⁴¹⁾	
	2–3 nm	HZO	10 nm	As-grown or 500 °C	PMA	TiN/TiN	MFM	2021	Qi et al. ⁵²⁾	
TiO ₂	1–5 nm	HZO	10 nm	400 °C	Deposition temperature of TE-TiN	TiN/TiN	MFM	2022	Koroleva et al. ⁵³⁾	
	1 nm	HZO	10 nm	500 °C		PMA	W/W	MFM	2024	Wang et al. ⁵⁴⁾
	1 nm	HZO	10 nm	450 °C		PMA	TiN/TiN	MFM	2024	Li et al. ⁴⁶⁾
	1 nm	HZO	10 nm	300 °C–600 °C		PMA	TiN/TiN	MFM	2025	Liu et al. ⁵⁵⁾
	1 nm	HZO	10 nm	600 °C		PMA	TiN/TiN	MFM	2020	Gaddam et al. ⁵⁶⁾
HfO ₂	10 nm	HZO	10 nm	600 °C	PDA	TiN/TiN	MFM	2020	Onaya et al. ³⁹⁾	
	1 nm	HZO	10 nm	300 °C–400 °C	PMA	TiN/TiN	MFM	2021	Gaddam et al. ⁴¹⁾	
	2 nm	HZO	12 nm	550 °C	PMA	TaN/Si	MFS	2021	Liu et al. ⁵⁷⁾	
	3 nm	HZO	15 nm	450 °C	PMA	TiN/Si	MFS	2022	Liu et al. ⁵⁸⁾	
	1 nm	HZO	4.5 or 9.5 nm	300 °C–500 °C	PMA	TiN/TiN	MFM	2023	Yu et al. ⁴³⁾	

Continued on next page.

Table I. Continued.

IL		HfO ₂ -based film		Annealing		TE/BE material	Device type	Year	References
Material	Thickness	Material	Thickness	Temperature	Annealing type				
HZO	1 nm	HZO	10 nm	450 °C	PMA	TiN/TiN	MFM	2024	Li et al. ⁴⁶⁾
	2 nm	HZO	10 nm	600 °C	PDA	TiN/TiN	MFM	2017	Onaya et al. ³⁴⁾
	2.2 nm	HZO	6.6 nm	550 °C–800 °C	Deposition temperature of HZO film	Pt/La _{0.67} Sr _{0.33} MnO ₃	MFM	2023	Song et al. ⁵⁹⁾
	2.2 nm	HZO	6.8 nm	550 °C	PMA	W/W or W/Si	MFM or MFS	2025	Park et al. ⁶⁰⁾
SiO ₂	1 nm	HZO	10 nm	300 °C–400 °C	PMA	TiN/TiN	MFM	2021	Gaddam et al. ⁴¹⁾
Ta ₂ O ₅	1–5 nm	HZO	10 nm	600 °C	PMA	TiN/TiN	MFM	2020	Gaddam et al. ⁶¹⁾
HfO _x N _y	2–200 nm	HZO	7–25 nm	500 °C	PMA	TiN/TiN	MFM	2022	Kim et al. ⁶²⁾

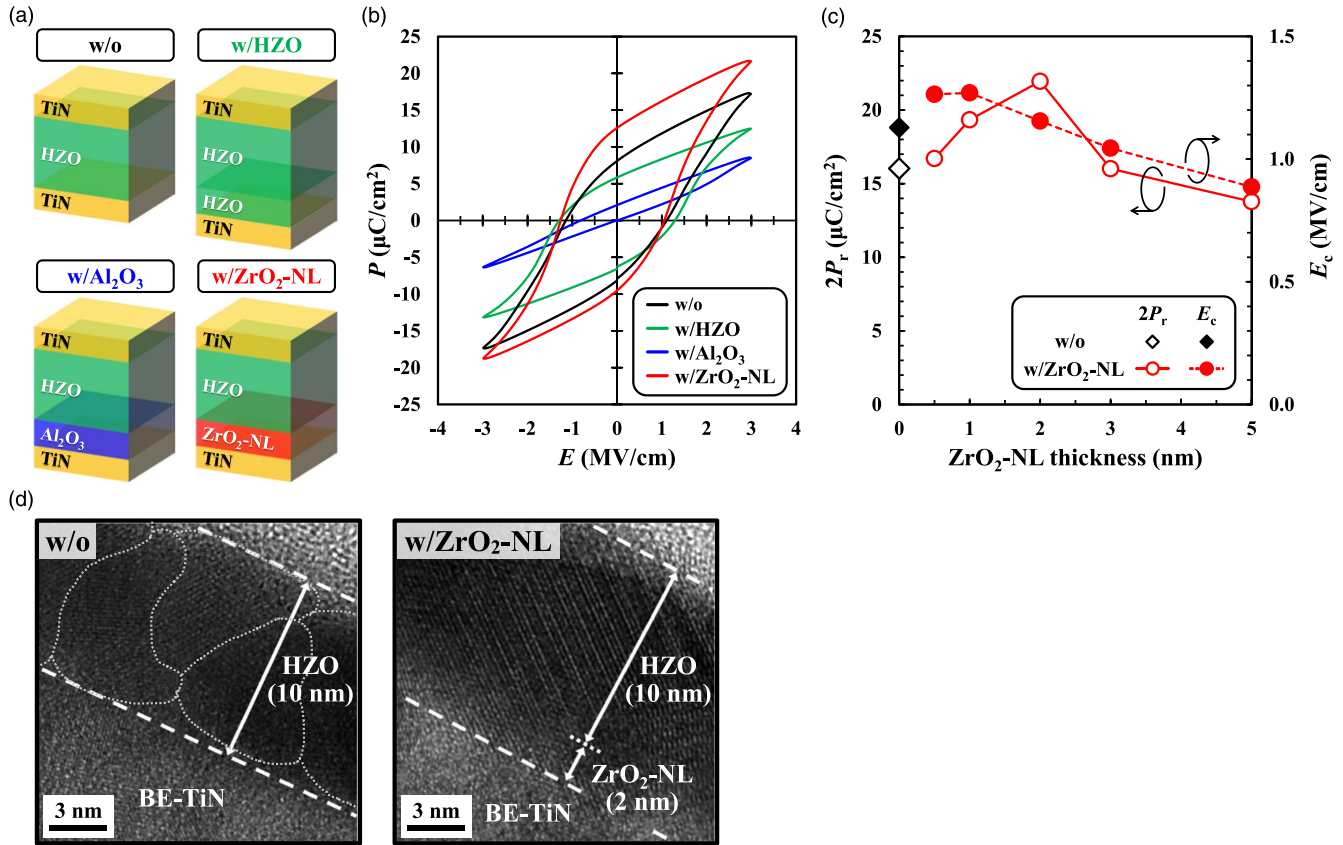


Fig. 2. (a) Schematics of four types of MFM capacitors: w/o, w/ HZO, w/ Al₂O₃, and w/ ZrO₂-NL capacitors. (b) P - E hysteresis loops for four types of MFM capacitors. (c) $2P_r$ and E_c values as functions of ZrO₂-NL thickness. (d) Cross-sectional TEM images of PDA-treated w/o and w/ ZrO₂-NL samples. Reproduced from Ref. 34 with permission of IOP Publishing. Copyright 2017 The Japan Society of Applied Physics.

a thickness of 2 nm was found to be uniformly formed on a TiN substrate and to have crystallized without an annealing process, as determined by cross-sectional transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (Fig. 1(b)). The ALD-ZrO₂ film was determined to be advantageous as an NL because the lattice constants for the O, T, and C phases in ZrO₂ well match those for the ferroelectric O phase in HfO₂. Thus, the ALD-ZrO₂ film is expected to promote the formation of the ferroelectric O phase as an NL in HZO films when an ALD-ZrO₂ film is inserted between the HZO film and the electrode.

Here, MFM capacitors were fabricated using three different ALD-ILs with different crystal structures: crystallized ZrO₂ (w/ZrO₂-NL), amorphous Al₂O₃ (w/Al₂O₃), and amorphous HZO (w/HZO), which were inserted between a 10-nm-thick amorphous HZO film and the BE-TiN (Fig. 2(a)). A TiN/HZO/TiN MFM capacitor without an ALD-IL (w/o) was also prepared as a reference. Post-deposition annealing (PDA) was performed at 600 °C for 1 min under a N₂ atmosphere before the formation of the TE-TiN. The $2P_r$ values extracted from polarization–electric field (P - E) hysteresis loops increased in the order w/Al₂O₃ ($2.1 \mu\text{C cm}^{-2}$) < w/HZO ($12.1 \mu\text{C cm}^{-2}$) < w/o ($16.0 \mu\text{C cm}^{-2}$) < w/ZrO₂-NL ($22.1 \mu\text{C cm}^{-2}$) (Fig. 2(b)). In addition, in the w/ZrO₂-NL case, the maximum $2P_r$ value was obtained when the thickness of the ZrO₂-NL was 2 nm (Fig. 2(c)). Notably, P - E measurements were carried out in the range from -3.0 to 3.0 MV cm^{-1} because the breakdown electric fields for the w/o, w/HZO, w/Al₂O₃, and w/ZrO₂-NL capacitors were 3.3, 3.1, 3.2, and 3.1 MV cm^{-1} , respectively,

as evaluated by leakage current density–electric field (J - E) measurements (data not shown). The w/Al₂O₃ and w/HZO capacitors fabricated using amorphous Al₂O₃ and HZO-ILs, respectively, did not show an improvement in $2P_r$ value compared with the w/o capacitor. In the w/Al₂O₃ case, the Al₂O₃-IL maintained an amorphous structure even after the PDA at 600 °C because of the higher crystallization onset temperature of Al₂O₃ ($>700 \text{ °C}$).⁷³ This result suggests that amorphous Al₂O₃-IL inhibited the crystallization and formation of the O phase in HZO films during the PDA process. In addition, most of the electric field (E) was applied not to the ferroelectric HZO film but to the Al₂O₃-IL, which led to a further reduction in the $2P_r$ value because the k value for amorphous Al₂O₃ ($k \approx 9$) is substantially lower than that for polycrystalline HZO ($20 \leq k \leq 40$).^{63,64,66,67} In the w/HZO case, the amorphous HZO film was crystallized after the PDA process but the $2P_r$ value did not improve. This lack of improvement in the $2P_r$ value might be attributable to enhanced formation of the stable M phase as a result of the increase in total thickness of the HZO films with additional HZO-IL.^{26,74–76} By contrast, the w/ZrO₂-NL capacitor fabricated using a crystallized ZrO₂-IL consisted predominantly of O/T/C phases and exhibited a $2P_r$ value approximately 1.4 times higher than that for the w/o capacitor.

Two possible roles of the crystallized ZrO₂-NL in enhancing the ferroelectricity of HZO films have been proposed. The first is that of a seed layer for the crystallization and formation of the ferroelectric O phase in HZO films.^{34,35}

Fig. 2(d) shows cross-sectional TEM images of PDA-treated

HZO/BE-TiN (w/o) and HZO/ZrO₂/BE-TiN (w/ZrO₂-NL) samples. For the w/o sample, the HZO film consisted of numerous separate grains with a size of 5–10 nm. For the w/ZrO₂-NL sample, on the other hand, no grain boundaries were observed between the HZO film and the ZrO₂-NL and the lattice fringes of the HZO film were aligned with those of the ZrO₂-NL. The ZrO₂-NL crystallized even after the ALD process and formed the O/T/C phases (Fig. 1), which have approximately the same lattice constant as the O phase of HZO. These results indicate that the amorphous HZO film was crystallized on the surface of the pre-crystallized ZrO₂-NL, leading to epitaxial-like grain growth of the HZO film with the O/T/C phases during the PDA process. Consequently, the HZO/ZrO₂-NL grain size (10–18 nm) is larger than that in the w/o case. A larger grain size is considered to promote phase transformation from the metastable O phase to the stable M phase as a result of the reduced influence of surface energy.^{26,77–80} On the other hand, on the basis of first-principles calculations, Huang et al. reported that the ZrO₂-NL effectively stabilizes the O phase in the HfO₂ film.⁸¹ Thus, the w/ZrO₂-NL sample maintained a higher fraction of O/T/C phases and exhibited a higher $2P_r$ value because of the crucial roles the ZrO₂-NL played in both the formation and stabilization of the O phase in HZO films. ZrO₂ thin films with an amorphous structure can be used as an IL. In this case, because the crystallization onset temperature for ZrO₂ is lower than that for HfO₂, the amorphous ZrO₂-IL crystallizes prior to HfO₂ during the annealing process, thereby potentially acting as a NL.

The second role of a ZrO₂-NL is that of a stressor layer for the formation of the O phase in HZO films during the PDA process, which is a result of a difference in thermal expansion coefficients between the ZrO₂-NL and the HZO films.^{9,41} As previously mentioned, Kim et al. reported that mechanical tensile stress during the annealing process is a key factor in promoting the formation of the metastable O phase.¹⁸ The thermal expansion coefficient for ZrO₂ ($10.3 \times 10^{-6} \text{ K}^{-1}$) is greater than that for HfO₂ ($6.5 \times 10^{-6} \text{ K}^{-1}$).^{68,82} Therefore, the ZrO₂-NL can induce tensile stress in the HZO film during the PDA process, originating from the difference in thermal expansion coefficients. To provide evidence supporting the effect of stress, Gaddam et al. investigated the relationship between the thermal expansion coefficient for ILs and the ferroelectricity of HZO films and found that the ZrO₂-NL successfully promoted the formation of the O phase in a HZO film.⁴¹ On the basis of the aforementioned experiments, we concluded that ALD-ZrO₂-NL enables crystal phase control in HfO₂-based films because of its two critical roles as a seed layer and a stressor layer.

As previously explained, a 2 nm thick ALD-ZrO₂-NL effectively improved the $2P_r$ value for a 10 nm thick HZO film (Fig. 2(c)). For ZrO₂-NL with a thickness up to 2 nm, the $2P_r$ value increased with increasing ZrO₂-NL thickness, possibly because the ALD-ZrO₂-NL, which has a polycrystalline structure on the BE-TiN, transitioned from island-like growth to a continuous layer as the number of ALD cycles increased. In addition, the mechanical tensile stress originating from the difference in thermal expansion coefficients could be enhanced during the PDA process because of the increasing ZrO₂-NL thickness. By contrast, when the

ZrO₂-NL thickness exceeded 2 nm, both the $2P_r$ value and the coercive electric field (E_c) decreased with increasing ZrO₂-NL thickness. Given that a ZrO₂ single layer generally exhibits antiferroelectric behavior, this decrease in the $2P_r$ and E_c values is attributed to an increased proportion of the antiferroelectric component of the ZrO₂-NL within the HZO/ZrO₂-NL stack. Therefore, to achieve superior ferroelectricity, the thicknesses of HfO₂-based films and ZrO₂-NLs are required to be carefully selected.

2.2. Effect of the insertion position of the ALD-ZrO₂-NL

The insertion position of the ALD-ZrO₂-NL also affects the crystallinity and ferroelectricity of HfO₂-based films. Four different HZO-based MFM capacitors were fabricated without (w/o) and with a bottom ZrO₂-NL (B-ZrO₂), top ZrO₂-NL (T-ZrO₂), and double ZrO₂-NLs (D-ZrO₂), as shown in Fig. 3(a). The thicknesses of the HZO film and ZrO₂-NL were 10 and 2 nm, respectively. PDA was carried out at 600 °C for 1 min under a N₂ atmosphere before the TE-TiN was formed. The $2P_r$ value for the MFM capacitors increased in the order w/o ($12 \mu\text{C cm}^{-2}$) < B-ZrO₂ ($15 \mu\text{C cm}^{-2}$) < T-ZrO₂ ($23 \mu\text{C cm}^{-2}$) < D-ZrO₂ ($29 \mu\text{C cm}^{-2}$). These values were extracted from the P - E hysteresis curves (Fig. 3(b)). The $2P_r$ values for the MFM capacitors were improved using the ZrO₂-NL. A comparison of the $2P_r$ values for the MFM capacitors fabricated using only a single ZrO₂-NL reveals that the T-ZrO₂ capacitor exhibited a higher $2P_r$ value than the B-ZrO₂ capacitor. Notably, the D-ZrO₂ capacitor with top and bottom ZrO₂-NLs showed the highest $2P_r$ value, which was approximately 2.4 times greater than that for the w/o capacitor.

To clarify the differences in $2P_r$ values for HZO films, we evaluated their crystallinity by TEM and XRD analysis (Figs. 3(c) and 3(d)). From cross-sectional TEM images, epitaxial-like grain growth between the HZO film and the ZrO₂-NLs was found to occur for the B-, T-, and D-ZrO₂ samples with ZrO₂-NLs during the PDA process; by contrast, random grain growth of the HZO film was observed for the w/o sample. In addition, for the D-ZrO₂ sample, grain boundaries were partially observed in the lateral direction in the HZO film; these grain boundaries are considered to be an interface where HZO grains growing from the top and bottom ZrO₂-NLs collided. A grazing-incidence XRD (GI-XRD) pattern showed overlapped diffraction peaks at $2\theta \approx 30.5^\circ$, which are related to a mixture of the O, T, and C phases (Fig. 3(d)); deconvolution of these peaks is difficult because of the extremely similar lattice constants for the O, T, and C phases and the limited resolution of conventional XRD instruments that use a laboratory-based X-ray source.¹⁰ To compare the crystal phase fraction for the HZO films for four types of MFM capacitors, the relative ratio of O/T/C phases ($r_{\text{O/T/C}}$) was estimated using the relation $r_{\text{O/T/C}} = A_{\text{O(111)}/\text{T(101)}/\text{C(111)}} / \{A_{\text{O(111)}/\text{T(101)}/\text{C(111)}} + A_{\text{M(-111)}} + A_{\text{M(111)}}\}$, where $A_{\text{O(111)}/\text{T(101)}/\text{C(111)}}$, $A_{\text{M(-111)}}$, and $A_{\text{M(111)}}$ are the integrated peak areas of O(111)/T(101)/C(111), M(-111), and M(111) from the GI-XRD patterns, respectively.³⁵ When ZrO₂-NLs were used, the $r_{\text{O/T/C}}$ increased in the order w/o (52%) < B-ZrO₂ (54%) < T-ZrO₂ (62%) < D-ZrO₂ (64%).

To investigate the relationship between the crystallinity and ferroelectricity of HZO films, we plotted the $2P_r$ values

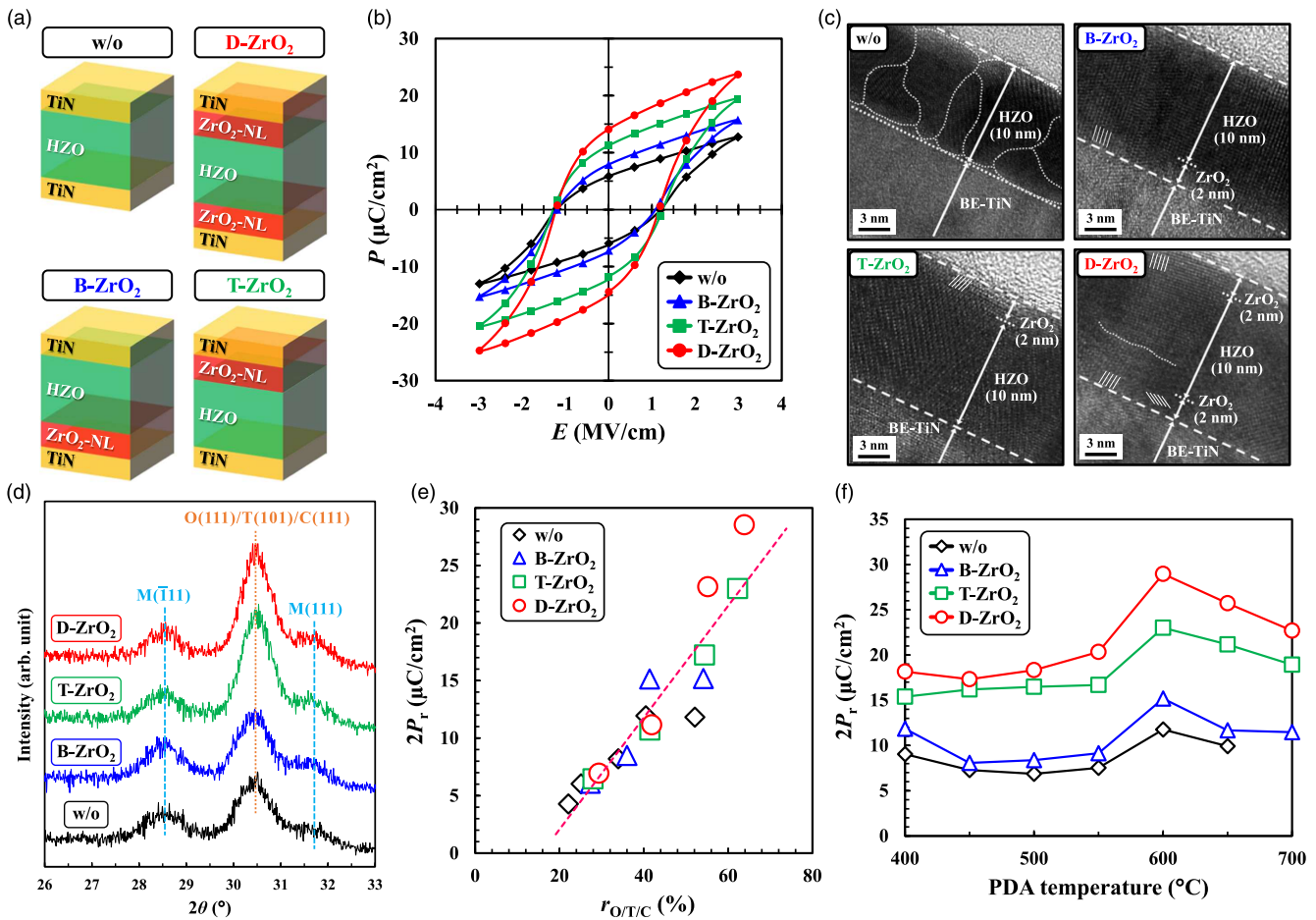


Fig. 3. (a) Schematics of four types of MFM capacitors: w/o, B-ZrO₂, T-ZrO₂, and D-ZrO₂ capacitors. (b) P - E hysteresis loops, (c) cross-sectional TEM images, and (d) GI-XRD patterns for four types of MFM capacitors. (e) Relationship between $r_{O/TC}$ and $2P_r$ value for four types of MFM capacitors as function of HZO thickness. (f) $2P_r$ value for four types of MFM capacitors as function of PDA temperature. Reproduced from Ref. 35 with permission of AIP Publishing, licensed under a Creative Commons Attribution (CC BY) license.

as a function of $r_{O/TC}$ (Fig. 3(e)). In this figure, the data for the four types of MFM capacitors are plotted as a function of the HZO thickness from 10 to 25 nm. A clear positive correlation is observed, indicating that the enhancement of the O/T/C phase fraction directly contributed to the improved $2P_r$ value, consistent with previously reported trends.⁷² In addition, although the $r_{O/TC}$ includes contributions from the non-ferroelectric T and C phases, the $2P_r$ value of $\sim 41 \mu\text{C cm}^{-2}$ estimated by extrapolating the horizontal axis of $r_{O/TC}$ to 100% is in reasonable agreement with the theoretical value ($40\text{--}53 \mu\text{C cm}^{-2}$) for randomly oriented polycrystalline HfO₂-based films on the basis of first-principles calculations.⁸³ This result suggests that these ferroelectric films predominantly consisted of the ferroelectric O phase rather than the non-ferroelectric T and C phases. As previously explained, the $2P_r$ and $r_{O/TC}$ values for the w/o sample are higher than those for the B-ZrO₂ sample because of the role the ZrO₂-NL plays in O/T/C phase formation. A comparison of the samples prepared using a single ZrO₂-NL reveals that the T-ZrO₂ sample exhibited a higher $2P_r$ and $r_{O/TC}$ than the B-ZrO₂ sample. Thin films are widely recognized as tending to crystallize preferentially from the surface rather than from the bulk region because of the lower activation energy for nucleation at the free surface. This behavior indicates that the top ZrO₂-NL plays a more dominant role than the bottom-ZrO₂-NL in determining the crystallinity of HZO

films, resulting in a higher $2P_r$ and $r_{O/TC}$ for the T-ZrO₂ sample. The D-ZrO₂ sample showed the highest $2P_r$ and $r_{O/TC}$ because of the effect of both top and bottom ZrO₂-NLs. On the basis of these results, we found that the crystallinity and ferroelectricity of HfO₂-based films were affected by the insertion position of ZrO₂-NLs, where both top and bottom ZrO₂-NLs promote O/T/C phase formation.

The dependence of the PDA process temperature on the ferroelectricity was also investigated (Fig. 3(f)). All of the MFM capacitors exhibited their highest $2P_r$ values when the PDA temperature was 600 °C. The D-ZrO₂ capacitors maintained a higher $2P_r$ value than the other capacitors for PDA temperatures of 400 °C–700 °C. In addition, for the D-ZrO₂ capacitor, a twofold higher $2P_r$ value ($18 \mu\text{C cm}^{-2}$) was obtained compared with that for the w/o capacitor ($9.0 \mu\text{C cm}^{-2}$) even at the low annealing temperature of 400 °C, which is compatible with the thermal budget of BEOL processes.

On the basis of these results, ZrO₂-NLs play a crucial role in promoting the formation of the O/T/C phases in HfO₂-based films; in particular, the D-ZrO₂ capacitor with both top and bottom ZrO₂-NLs exhibited the highest $2P_r$ and $r_{O/TC}$.

2.3. CET scaling using ALD-ZrO₂-NL

Various dopants for ferroelectric HfO₂-based materials have been reported, including Si,¹⁾ Al,^{84,85)} and Zr.²⁾ Among such doped materials, the HZO film consisting of HfO₂ and ZrO₂

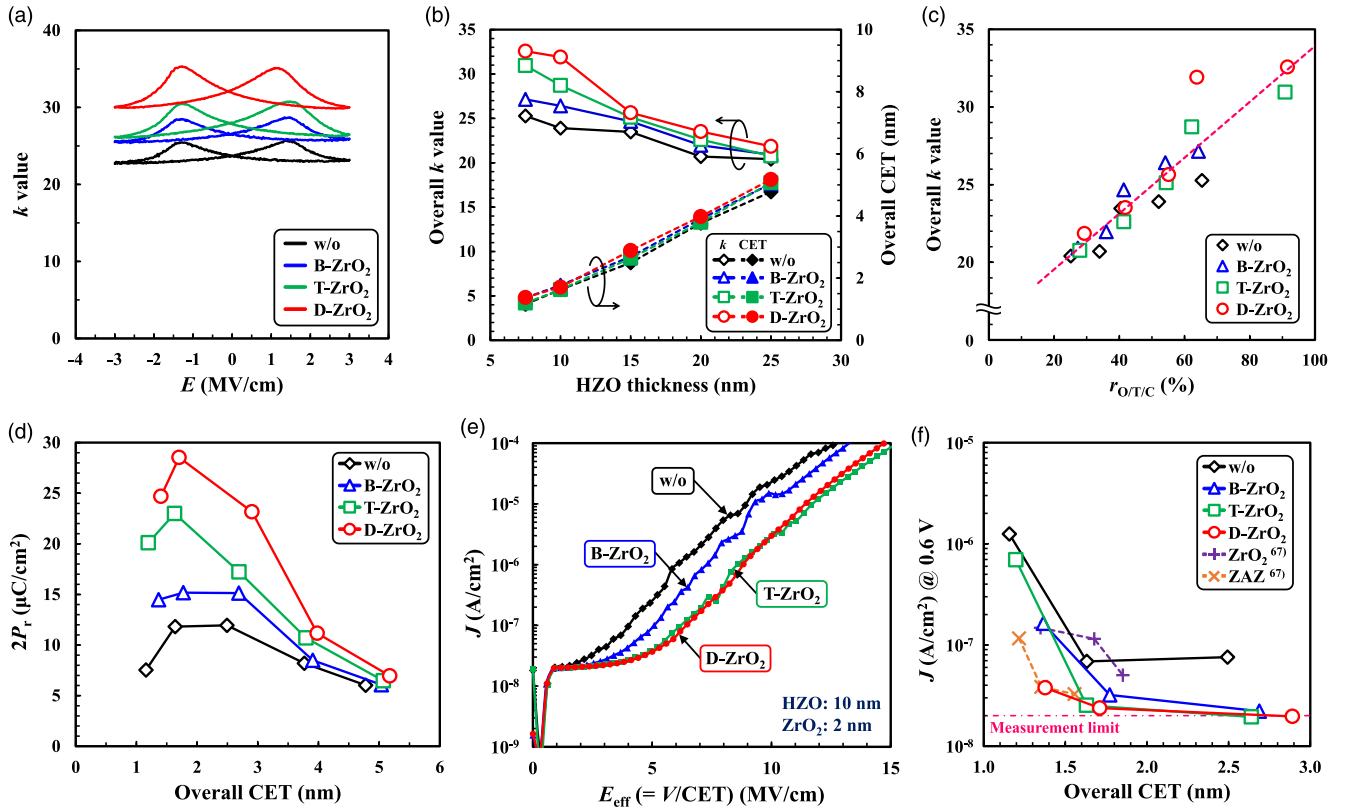


Fig. 4. (a) k - E properties of four types of MFM capacitors: w/o, B-ZrO₂, T-ZrO₂, and D-ZrO₂ capacitors, with 10-nm-thick HZO film. (b) Overall k and CET values for four types of MFM capacitors as functions of HZO thickness. (c) Relationship between $r_{O/T/C}$ and overall k value and (d) relationship between overall CET and $2P_r$ value for four types of MFM capacitors as function of HZO thickness. (e) J - E_{eff} characteristics of four types of MFM capacitors with 10 nm thick HZO film. (f) Relationship between overall CET value and J value at 0.6 V for four types of MFM capacitors as function of HZO thickness from 7.5 to 15 nm. The reference samples of ZrO₂- and ZAZ-based MIM capacitors were compared with these four types of MFM capacitors.⁶⁷⁾ © The Electrochemical Society. Reproduced from Ref. 95 with permission of IOP Publishing. All rights reserved.

with a higher k value of approximately 20–40 is expected to exhibit a low CET value, whereas the lower k values for SiO₂ and Al₂O₃ of 3.9 and ~ 9 , respectively, may lead to an increase of the CET value for Si- and Al-doped HfO₂ films.^{63,64,66,67)} HfO₂ and ZrO₂ are well known to typically form four crystal phases of M, O, T, and C phases. In addition, the O, T, and C phases of HfO₂ and ZrO₂ exhibit k values greater than that for the stable M phase because the k value increases with increasing density according to the Clausius–Mossotti relation.⁸⁶⁾ Thus, the formation of the HZO film with the O/T/C phases improves not only its ferroelectricity but also its k value, thereby leading to a low CET value. In addition, the reduction of the CET value for ferroelectric HZO films allows for a relatively greater physical thickness, which consequently leads to a reduction in the leakage current. In this subsection, we therefore discuss the electrical characteristics (e.g. k , CET, leakage current, and $2P_r$) of the ferroelectric HZO films fabricated using the top and bottom ZrO₂-NLs.

The w/o, B-ZrO₂, T-ZrO₂, and D-ZrO₂ MFM capacitors were fabricated with different HZO thicknesses from 7.5 to 25 nm while the ZrO₂-NL thickness was maintained at 2 nm (Fig. 3(a)). The k - E properties of the four types of MFM capacitors with a 10 nm thick HZO film are shown in Fig. 4(a). The k value was extracted using the capacitance at 0 MV cm⁻¹. All capacitors exhibited butterfly-like hysteresis loops, which are a typical characteristic of ferroelectric materials. The overall k value for the ferroelectric film that

included both the HZO film and the ZrO₂-NLs increased in the order w/o (24) < B-ZrO₂ (26) < T-ZrO₂ (29) < D-ZrO₂ (32). This order is the same as that for the $2P_r$ values (Fig. 3(b)), indicating that the $r_{O/T/C}$ extracted from GI-XRD patterns is also correlated with the k value. The D-ZrO₂ capacitor exhibited the highest k value, which was approximately 1.3 times higher than that for the w/o capacitor.

Figure 4(b) shows the overall k and CET values for the four types of MFM capacitors as a function of the HZO thickness. In addition, the relationship between the $r_{O/T/C}$ and the overall k value as a function of the HZO thickness is shown in Fig. 4(c). Various k values were obtained by changing the insertion position of the ZrO₂-NLs and the thickness of the HZO film; however, the overall k value for all of the capacitors increased linearly with increasing $r_{O/T/C}$. These results indicate that the k value is closely correlated with the fraction of the O/T/C phases in the HZO film as well as with the $2P_r$ value. The B-, T-, and D-ZrO₂ capacitors with the ZrO₂-NLs exhibited higher k values than the w/o capacitor because of a higher $r_{O/T/C}$. The k value for all of the capacitors linearly decreased with increasing HZO thickness because a larger grain size caused by the thicker HZO films promotes the formation of the stable M phase rather than the O/T/C phases.^{26,74–76)} Consequently, the CET value for all of the MFM capacitors increased linearly with increasing HZO thickness. Notably, the B-, T-, and D-ZrO₂ capacitors exhibited approximately the same CET values as the w/o capacitor despite the additional thickness of the ZrO₂-NLs,

especially in the HZO thickness region <15 nm, because of their higher k values. For the capacitors with a 10 nm thick HZO film, the overall CET value for the D-ZrO₂ capacitor (1.7 nm) was approximately the same as that for the w/o capacitor (1.6 nm), whereas the thickness of the overall ferroelectric film (14 nm) was 40% greater than that for the w/o capacitor (10 nm).

Figure 4(d) shows the relationship between the CET and $2P_r$ value for the overall ferroelectric film for four types of MFM capacitors. The four types of MFM capacitors exhibited higher $2P_r$ values when the HZO thickness was <15 nm; however, the $2P_r$ value decreased dramatically with increasing HZO thickness because of a lower $r_{O/T/C}$. Notably, the D-ZrO₂ capacitor with a 10 nm thick HZO film achieved the highest $2P_r$ value ($29 \mu\text{C cm}^{-2}$) among the four types of MFM capacitors. The $2P_r$ values for the four types of MFM capacitors decreased with decreasing HZO thickness from 10 to 7.5 nm. This behavior might be attributable to the HZO film forming more T or C phase than O phase. On the other hand, the D-ZrO₂ capacitor with a 7.5-nm-thick HZO film (CET = 1.4 nm) exhibited a $2P_r$ value ($25 \mu\text{C cm}^{-2}$) approximately 3.3 times greater than that ($7.5 \mu\text{C cm}^{-2}$) for the w/o capacitor (CET = 1.2 nm).

To further demonstrate the effects of the ZrO₂-NL, the leakage current density–effective electric field (J – E_{eff}) characteristics of four types of MFM capacitors with a 10 nm thick HZO film are shown in Fig. 4(e). The E_{eff} was calculated using the applied voltage and the overall CET value. The J values for the MFM capacitor fabricated using the ZrO₂-NL were lower than that for the w/o capacitor. The E_{eff} at $10^{-7} \text{ A cm}^{-2}$ increased in the order w/o (4.0 MV cm^{-1}) $<$ B-ZrO₂ (5.1 MV cm^{-1}) $<$ T-ZrO₂ (6.1 MV cm^{-1}) $<$ D-ZrO₂ (6.4 MV cm^{-1}). The E_{eff} for the T-ZrO₂ capacitor was greater than that for the B-ZrO₂ capacitor even though the capacitors had the same total physical thickness of 12 nm. This greater E_{eff} for the T-ZrO₂ capacitor is attributed to its lower CET value (1.8 nm) compared with that for the B-ZrO₂ capacitor (1.6 nm), which is a result of the different roles of the top and bottom ZrO₂-NLs, as discussed in the previous subsection. The J properties of the T- and D-ZrO₂ capacitors were approximately the same even though the physical thickness of the D-ZrO₂ capacitor (14 nm) was greater than that of the T-ZrO₂ capacitor (12 nm). This result can be explained by the minimal difference in CET values between the T- and D-ZrO₂ capacitors (1.6 and 1.7 nm, respectively) as a result of the higher k value for the D-ZrO₂ capacitor.

Finally, the relationship between the overall CET value and the J value at 0.6 V for four types of MFM capacitors as a function of HZO thickness from 7.5 to 15 nm is shown in Fig. 4(f). For comparison, data for metal–insulator–metal capacitors with a ZrO₂ single layer (ZrO₂) ($k = 28$) and ZrO₂/Al₂O₃/ZrO₂ multilayers (ZAZ) ($21 \leq k \leq 26$), which are typically used as insulators for dynamic random access memory capacitors, are also plotted.⁶⁷⁾ The J values for the B-, T-, and D-ZrO₂ capacitors were lower than those for the w/o capacitor with almost the same profiles as the ZrO₂ capacitor. In addition, the D-ZrO₂ capacitors showed lower J values than the B- and T-ZrO₂ capacitors. These results are attributed to a greater thickness of the overall ferroelectric films with both the top and bottom ZrO₂-NLs. The D-ZrO₂

capacitor with a 7.5 nm thick HZO film exhibited a low J value of $3.8 \times 10^{-8} \text{ A cm}^{-2}$ while maintaining a lower CET value of 1.4 nm, which is comparable to that for the ZAZ capacitor. This lower CET value was achieved by maintaining a higher k value as a result of the ZrO₂-NL effect, even as the physical thickness increased. On the basis of these experimental data, we concluded that electrical properties such as the $2P_r$, k , and J of the HfO₂-based films were substantially improved by the incorporation of the top and bottom ZrO₂-NLs.

3. Improvement of reliability using ALD-ZrO₂-NLs

Since the first report of ferroelectric HfO₂-based materials in 2011, these materials have moved closer to being used in practical applications. Currently, to ensure reliability of HfO₂-based ferroelectric devices, numerous researchers are focusing on the critical challenges regarding reliability. To achieve a higher breakdown voltage (V_{bd}) and superior endurance properties while maintaining high $2P_r$ values, MFM capacitors with thick HZO films were fabricated using ALD-ZrO₂-NLs.

For the fabrication of HZO-based MFM capacitors, a top ZrO₂-NL was inserted between the HZO film and TE-TiN and the thickness of the HZO films was varied from 10 to 30 nm. To achieve a higher V_{bd} , a thick top ZrO₂-NL with a thickness of 10 nm was used because HZO-based MFM capacitors with a 10 nm thick top ZrO₂-NL maintained a high $2P_r$ value while suppressing the influence of the antiferroelectric behavior of ZrO₂ according to the relationship between the $2P_r$ value and ZrO₂-NL thickness (data not shown).³⁸⁾ A PDA process was performed at 600 °C for 1 min under a N₂ atmosphere before the formation of the TE-TiN. The MFM capacitors with a HZO single film (w/o) and HZO/ZrO₂-NL bilayer (w/ZrO₂-NL) are represented as “HZ#” and “HZ#Z#,” respectively, where HZ or Z and the attached number represent the film type and thickness, respectively. For example, HZ20Z10 represents an MFM capacitor with bilayer consisting of a 10 nm thick ZrO₂-NL on top of a 20 nm thick HZO film.

Figure 5(a) shows P – E hysteresis loops for the w/o and w/ZrO₂-NL MFM capacitors. The relationship between the total thickness and $2P_r$ values extracted from these P – E hysteresis loops is summarized in Fig. 5(b). For the w/o capacitor cases, the $2P_r$ value was $10 \mu\text{C cm}^{-2}$ for the HZ10 capacitor; however, the $2P_r$ value decreased substantially as the HZO thickness increased, consistent with previously reported trends.^{26,74–76)} Notably, the $2P_r$ value for the HZ25 capacitor is approximately half that for the HZ10 capacitor. This low $2P_r$ value is attributed to a decrease in the formation of the O phase and a concomitant increase in the fraction of the stable M phase with increasing thickness of the HZO films, as evaluated by GI-XRD analysis (data not shown). As the grain size increases with increasing thickness of the polycrystalline HZO films, a phase transformation from the metastable O phase to the stable M phase typically occurs because of the diminishing contribution of surface energy.^{26,77–80)} This mechanism makes simultaneously achieving both increased HZO thickness and robust ferroelectricity difficult. For the w/ZrO₂-NL capacitor cases, the HZ10Z10 capacitor exhibited a hybrid hysteresis loop with a mixture of ferroelectricity and antiferroelectricity because of

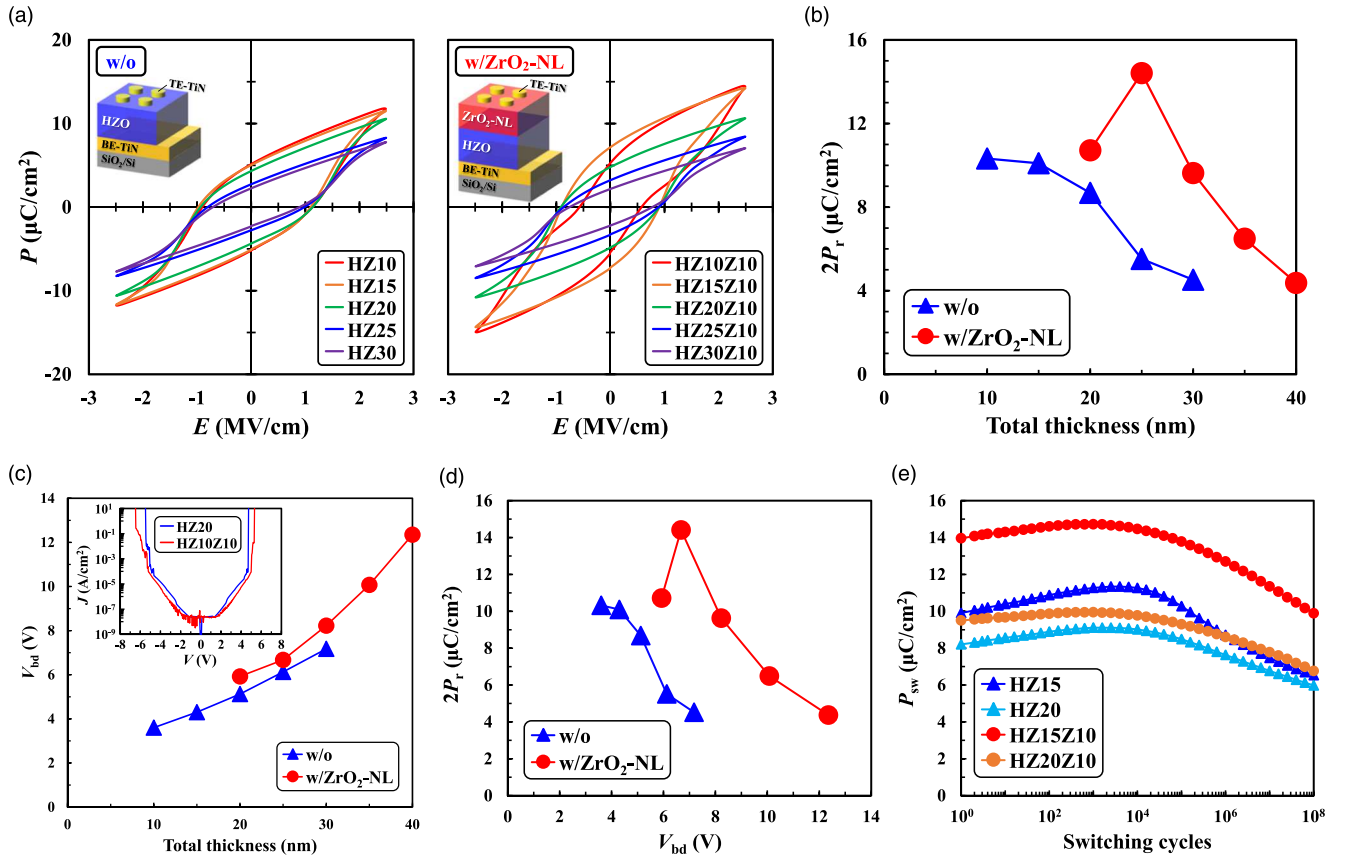


Fig. 5. (a) P - E hysteresis loops for w/o and w/ZrO₂-NL capacitors. (b) $2P_r$ values and (c) V_{bd} , extracted from J - V characteristics shown in inset, of w/o and w/ZrO₂-NL capacitors as function of HZO thickness. (d) Relationship between V_{bd} and $2P_r$ values for w/o and w/ZrO₂-NL capacitors. (e) Endurance properties of HZ15 and HZ20 capacitors for w/o capacitor cases and of HZ15Z10 and HZ20Z10 capacitors for w/ZrO₂-NL capacitor cases, as evaluated by PUND measurements. Reproduced from Ref. 38 with permission of AIP Publishing.

a higher proportion of antiferroelectric ZrO₂, resulting in a small $2P_r$ value. On the other hand, clear hysteresis loops were observed when the HZO thickness was increased to 15 nm or more. Notably, the HZ15Z10 capacitor achieved a maximal $2P_r$ value of $14 \mu\text{C cm}^{-2}$, which is higher than that for the HZ10 capacitor ($10 \mu\text{C cm}^{-2}$), even though the HZ15Z10 capacitor had a relatively large total thickness of 25 nm. This result suggests that the ZrO₂-NL could also exhibit ferroelectricity when the thickness ratio between the HZO film and the ZrO₂-NL was properly adjusted. At the same total thickness of 25 nm, the $2P_r$ value for the HZ15Z10 capacitor ($14 \mu\text{C cm}^{-2}$) was approximately 2.5 times higher than that for the HZ25 capacitor ($5.5 \mu\text{C cm}^{-2}$). Even for the w/ZrO₂-NL capacitors, a decrease in $2P_r$ value with increasing HZO thickness was unavoidable; however, the w/ZrO₂-NL capacitors maintained a higher $2P_r$ value than the w/o capacitors. Thus, the ALD-ZrO₂-NL enabled an increase in HZO thickness without compromising its high $2P_r$ value.

Figure 5(c) shows the relationship between the total thickness and the V_{bd} , which was extracted from the J - V characteristics shown in the inset, for the w/o and w/ZrO₂-NL capacitors. The V_{bd} for the HZ10 capacitor was 3.6 V ($E = 3.6 \text{ MV cm}^{-1}$), which is consistent with the typically reported breakdown E for HZO films ($3\text{--}4 \text{ MV cm}^{-1}$).²⁵ For both types of MFM capacitors, V_{bd} increased monotonically with increasing HZO thickness. The relationship between the V_{bd} and the $2P_r$ value for both capacitors, as obtained from

Figs. 5(a) and 5(c), is shown in Fig. 5(d). The profile for the w/ZrO₂-NL capacitors is shifted toward the higher V_{bd} region compared with that for the w/o capacitors. In particular, a comparison of capacitors with the same HZO thickness of 15 nm reveals that the $2P_r$ value and V_{bd} for the HZ15Z10 capacitor ($14 \mu\text{C cm}^{-2}$ and 6.7 V, respectively) were approximately 1.4 and 1.6 times higher than those for the HZ15 capacitor ($10 \mu\text{C cm}^{-2}$ and 4.3 V, respectively). These findings demonstrate that both a higher $2P_r$ and a higher V_{bd} can be achieved by thick HZO films fabricated using the ALD-ZrO₂-NL.

We next investigated the endurance properties of these capacitors, which remain a major challenge for their use in practical devices. Figure 5(e) shows the endurance properties of the HZ15 and HZ20 capacitors for the w/o capacitor cases and the HZ15Z10 and HZ20Z10 capacitors for the w/ZrO₂-NL capacitor cases, as evaluated by positive-up negative-down measurements. The switching polarization (P_{sw}) for the HZ15 and HZ20 capacitors clearly increased because of the wake-up effect up to $\sim 10^4$ cycles, reaching values approximately 15% and 11% higher than initial P_{sw} values of these capacitors, respectively. By contrast, the HZ15Z10 and HZ20Z10 capacitors with the ZrO₂-NL showed minimal wake-up, with an increase rate of less than 5%. The wake-up effect has been reported to originate from a field-induced phase transformation from the non-ferroelectric phase to the ferroelectric O phase.^{29,87–90} Thus, the suppressed increase rate during wake-up field cycling for

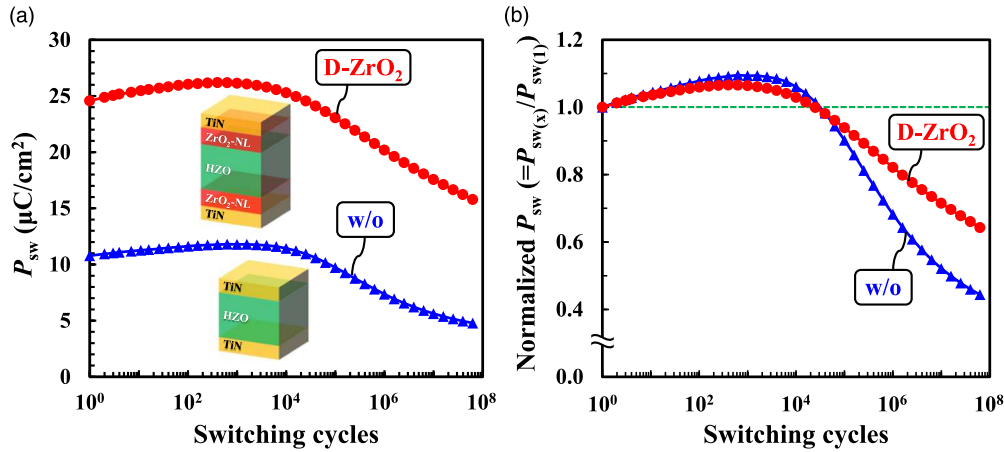


Fig. 6. (a) Endurance properties and (b) normalized P_{sw} values for w/o and D-ZrO₂ MFM capacitors with HZO and ZrO₂-NL thicknesses of 10 and 2 nm, respectively.

the HZ15Z10 and HZ20Z10 capacitors is attributed to a higher initial fraction of the O phase compared with that in the HZ15 and HZ20 capacitors, as evaluated by GI-XRD analysis (data not shown).³⁸⁾ In addition, the wake-up effect is speculatively attributed to domain depinning induced mainly by the redistribution of V_O , which are generally formed around grain boundaries and interfaces between the HZO film and TiN electrodes.^{29,91,92)} Therefore, we considered that larger grains, formed through the epitaxial-like grain growth of the HZO film on the ZrO₂-NL for the w/ZrO₂-NL capacitors, reduced the density of grain boundaries, thereby suppressing the increase in the P_{sw} caused by the wake-up effect. Subsequent to the wake-up state, a fatigue phenomenon (i.e. the degradation of P_{sw} with increasing number of switching cycles) were observed. The P_{sw} values for the HZ15 and HZ20 capacitors at 10^8 cycles decreased by 42% and 34%, respectively, compared with their peak values at 10^4 wake-up cycles. By contrast, the reduction rate for the P_{sw} value from 10^4 to 10^8 cycles for the HZ15Z10 and HZ20Z10 capacitors was approximately 30%, indicating that the fatigue for the w/ZrO₂-NL capacitors with the ALD-ZrO₂-NL was suppressed compared with that for the w/o capacitors. New defects, such as V_O , have been reported to be preferentially generated along grain boundaries during field cycling, leading to domain-pinning-induced degradation of ferroelectricity.^{29,93)} For the w/ZrO₂-NL capacitors, the insertion of the ZrO₂-NL promoted continuous grain growth across the HZO film and the ZrO₂-NL, leading to an increase in grain size. This is considered to have reduced the density of grain boundaries, thereby suppressing the degradation of the P_{sw} values. This interpretation is also consistent with the observation that the P_{sw} degradation was suppressed in the HZ20 capacitor with a thicker HZO film (which causes an increase in the grain size) compared with that in the HZ15 capacitor. In addition, Onaya et al. reported that one of the origins of V_O formation in HZO films is the field-induced interface reaction, where oxygen atoms are scavenged from the HZO film into TiN electrodes.^{31–33,94)} Furthermore, the MFM capacitor with the top and bottom ZrO₂-NLs (D-ZrO₂) showed higher fatigue resistance than that without the ZrO₂-NL (w/o) because the ALD-ZrO₂-NL could function as a blocking layer for oxygen diffusion, supporting the suppression of such

interface reactions during field cycling (Figs. 6(a) and 6(b)).^{32,95)} Accordingly, the ZrO₂-NL was considered to further effectively suppress P_{sw} degradation for the w/ZrO₂-NL capacitors. These findings indicate that the ALD-ZrO₂-NL is highly effective in improving reliability as well as in promoting formation of the O phase in HfO₂-based thin films.

4. Low-temperature fabrication process using ALD-ZrO₂-NLs

Recently, fabrication processes with a low thermal budget for HfO₂-based thin films have attracted widespread attention in attempts to enhance the versatility of these films for various applications such as BEOL integration and flexible devices with thermally sensitive substrates.^{8–11,96)} In addition, low-temperature fabrication can effectively suppress the formation of unexpected ILs between HfO₂-based thin films and substrates or electrodes. In particular, the formation of a thick and low quality SiO₂-IL between the HfO₂-based film and the Si substrate is a critical issue for the fabrication of ferroelectric HfO₂-based FeFETs because such SiO₂-ILs severely degrade device performance and reliability.^{24,97–99)} In previous research, Onaya et al. reported the relationship between process temperature and SiO₂-IL formation for ALD-HZO/SiO₂-IL/Si samples evaluated using X-ray photoelectron spectroscopy analysis (Fig. 7(a)).^{9,100)} The peak attributed to Si–O bonds at ~ 103.5 eV was negligibly small even after the ALD growth of the HZO film at 300 °C, showing a peak area comparable to that for a Si substrate after treatment with buffered hydrofluoric acid. Similarly, the peak area remained equivalent to that for the as-grown sample after the post-metallization annealing (PMA) process at 300 °C. By contrast, when the PMA temperature was 400 °C or greater, the Si–O peak area increased linearly with increasing PMA temperature. These results indicate that no substantial growth of the SiO₂-IL occurs during the fabrication process when both the ALD and the annealing temperature are 300 °C or less. In addition, cross-sectional TEM images reveal that a SiO₂-IL with a thickness of one or two monolayers (0.3–0.6 nm) was formed between the HZO film and the Si substrate after the PMA process at 300 °C (Fig. 7(b)). This SiO₂-IL is remarkably thin compared with those typically reported in the literature (≥ 1 nm).^{101–105)}

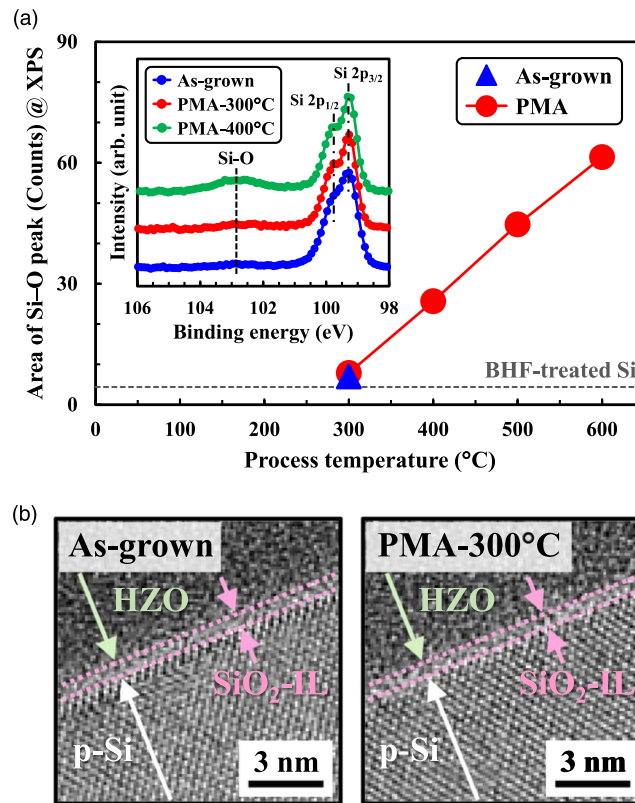


Fig. 7. (a) Relationship between process temperature and area of Si-O peak in XPS Si 2p spectra for as-grown and PMA-treated ALD-HZO/SiO₂-IL/Si samples. The inset shows XPS spectra for the Si 2p core level. (b) Cross-sectional TEM images of as-grown and 300 °C-PMA-treated ALD-HZO/SiO₂-IL/Si samples. Reproduced from Ref. 9 with permission of AIP Publishing, licensed under a Creative Commons Attribution (CC BY) license.

On the basis of this background, a 300 °C PMA process was carried out following the fabrication of TE-TiN to fabricate an MFS structure, which is a fundamental structure of FeFETs. In addition, to promote the crystallization and formation of the O phase and enhance the fatigue resistance, the ALD-ZrO₂-NL was integrated into the HZO-based MFS structures. Figure 8(a) shows cross-sectional TEM images of the TiN/HZO (10 nm)/SiO₂-IL/p⁺-Si (w/o) and TiN/ZrO₂-NL (10 nm)/HZO (10 nm)/SiO₂-IL/p⁺-Si (ZrO₂-10 nm) MFS capacitors after the PMA process at 300 °C. The GI-XRD patterns for both capacitors are shown in Fig. 8(b). Notably, a suppressed SiO₂-IL with a thickness of one or two monolayers (0.3–0.6 nm) for both capacitors was formed between the HZO film and the Si substrate, consistent with the results in Fig. 7. For the w/o capacitor, a few nanocrystals with a grain size of 5–10 nm partially formed in the HZO film, whereas most of the film remained amorphous after the PMA process at 300 °C. This result is attributed to the thermal expansion coefficient for Si ($2.5 \times 10^{-6} \text{ K}^{-1}$) being smaller than that for TiN ($9.4 \times 10^{-6} \text{ K}^{-1}$), whereas the HZO film sandwiched with TE- and BE-TiN was crystallized even after the PMA process at 300 °C.^{10,11,19,82} On the other hand, the HZO film in the ZrO₂-10 nm capacitor was fully crystallized with the same orientation as the ZrO₂ grains and the grain size was 10–20 nm. In addition, the O/T/C phases were dominantly formed for the ZrO₂-10 nm capacitor. Consequently, a higher $2P_r$ value was obtained for the ZrO₂-10 nm capacitor ($15 \mu\text{C cm}^{-2}$) than for the w/o capacitor ($2.2 \mu\text{C cm}^{-2}$), as shown in Fig. 8(c). Furthermore, the ZrO₂-10 nm capacitor exhibited a higher $2P_r$ value than the 2 nm thick ZrO₂-NL

(ZrO₂-2 nm). This result might be attributable to a thicker ZrO₂-NL enhancing the tensile stress resulting from the differences in the thermal expansion coefficient during the PMA process, which promotes the crystallization and formation of the O phase in the HZO film.^{18–22,106} These results indicate that the ZrO₂-NL plays a critical role in the crystallization and formation of the ferroelectric O phase of HZO films during the low-temperature PMA process at 300 °C, even on a Si substrate. Notably, the fabrication temperature of 300 °C achieved in this work is considerably lower than those typically reported in previous studies ($\geq 400 \text{ °C}$).^{8,11,24} The endurance properties of the capacitors were also evaluated (Fig. 8(d)). No wake-up effect was observed for the ZrO₂-2 nm and ZrO₂-10 nm capacitors, whereas the P_{sw} value for the w/o capacitor clearly increased with increasing number of switching cycles up to $\sim 10^3$ cycles. These wake-up-free characteristics are attributable to the preferential formation of the O phase and to the reduced grain boundary density resulting from the increase in grain size due to the ZrO₂-NL effect, as noted previously.⁹ In addition, the degradation of the P_{sw} value was suppressed compared with that observed for the w/o capacitor because of the role the ZrO₂-NL played in the growth of larger grains and because the ZrO₂-NL as a blocking layer prevented oxygen movement at the TE-TiN/HZO interface, as explained previously.^{9,31,32} On the basis of these results, we found that wake-up-free properties and higher fatigue resistance, as well as superior ferroelectricity for HZO-based MFS capacitors, were achieved using the ZrO₂-NL, even at a low thermal budget of 300 °C.

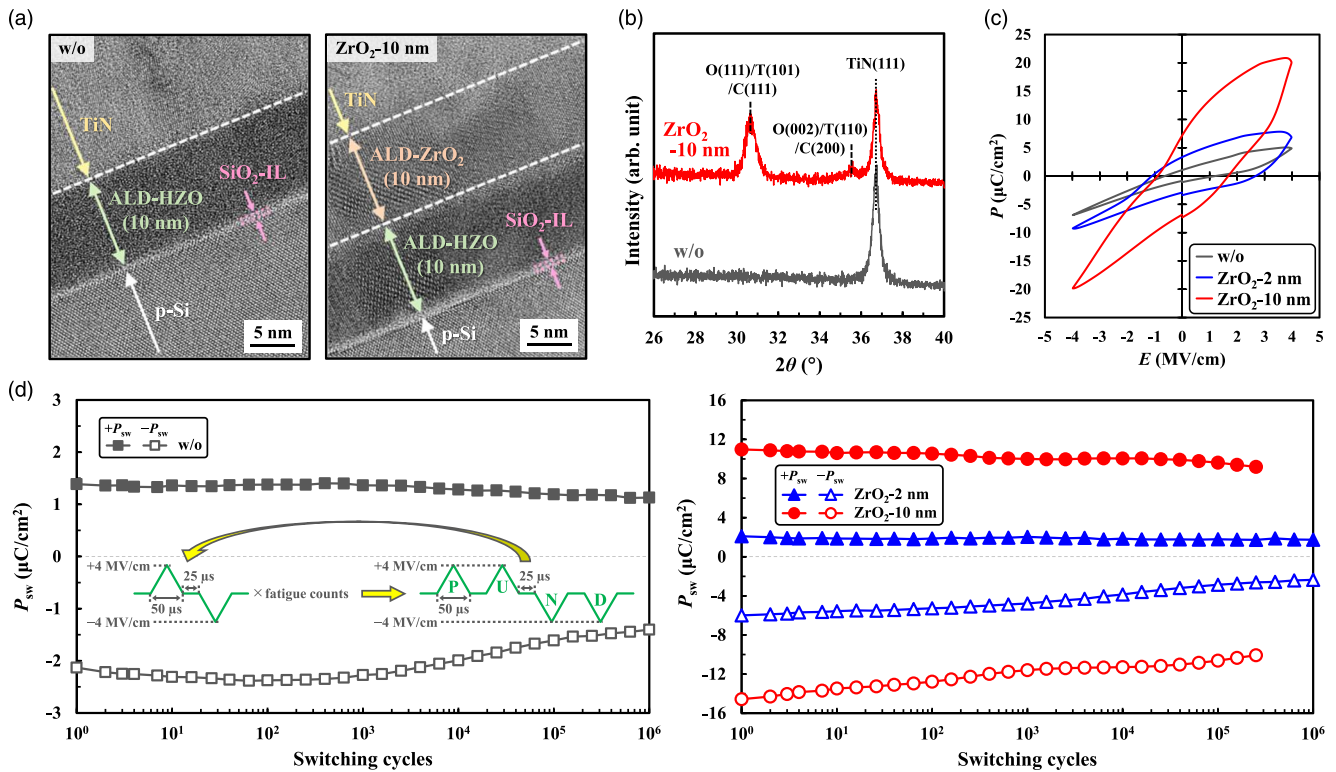


Fig. 8. (a) Cross-sectional TEM images and (b) GI-XRD patterns for w/o and ZrO₂-10 nm MFS capacitors after PMA process at 300 °C. (c) P - E hysteresis loops and (d) endurance properties of w/o, ZrO₂-2 nm, and ZrO₂-10 nm capacitors. Reproduced from Ref. 9 with the permission of AIP Publishing, licensed under a Creative Commons Attribution (CC BY) license.

5. Conclusions

Engineering of the interface between ferroelectric films and electrodes has attracted considerable attention for the practical application of HfO₂-based ferroelectric devices. In the present study, we focused on the fabrication of HfO₂-based thin films using ALD-ZrO₂-NLs inserted between a ferroelectric film and electrodes. The HZO films fabricated using ALD-ZrO₂-NLs promoted the formation of and stabilized the ferroelectric O phase, resulting in high $2P_r$ values. The roles of the ALD-ZrO₂-NLs in controlling the crystal phase of HZO films can be explained by two primary mechanisms. First, the ALD-ZrO₂-NLs were crystallized even after the ALD process, forming crystal phases whose lattices well match that of the ferroelectric O phase of HfO₂, whereas HfO₂-based thin films typically formed an amorphous structure. Thus, the ALD-ZrO₂-NL serves as a seed layer that promotes the crystallization and formation of the O phase in HfO₂-based thin films during annealing processes. Second, the ALD-ZrO₂-NL is considered to play a role as a stressor layer: the difference in thermal expansion coefficients between HfO₂ and ZrO₂ leads to mechanical tensile stress on HfO₂-based thin films during an annealing process, thereby promoting the formation of the ferroelectric O phase.

The effects of the ALD-ZrO₂-NL were found to vary depending on their insertion position. The top ZrO₂-NL inserted at the TE-TiN/HZO interface is more effective for the O phase formation in HfO₂-based thin films than the bottom ZrO₂-NL inserted at the BE-TiN/HZO interface. Notably, the HZO films fabricated using a combination of both the top and bottom ZrO₂-NLs exhibited a more pronounced O phase formation and higher $2P_r$ values compared with films fabricated using either the top or bottom

ZrO₂-NL. A higher k value was also obtained because of the formation of a larger portion of the O/T/C phases, resulting in a lower CET value. As a result, when ALD-ZrO₂-NLs were used, a lower J value was achieved while maintaining a low CET value, even in cases of a thicker ferroelectric film. In addition, by incorporating the ALD-ZrO₂-NL, the typical degradation of $2P_r$ values with increasing HfO₂-based film thickness was successfully suppressed, allowing for robust $2P_r$ values even in thicker films with a high V_{bd} . With respect to the endurance properties of HfO₂-based ferroelectric devices, the insertion of ALD-ZrO₂-NLs led to superior fatigue resistance because of the reduced grain boundary density resulting from the growth of larger grains; it also led to the prevention of interface reactions during field cycling. Low-temperature fabrication of the HZO films at 300 °C was also demonstrated using the ALD-ZrO₂-NL, resulting in the suppression of growth of the SiO₂-IL with a thickness of one or two monolayers (0.3–0.6 nm) at the HZO film and the Si substrate.

On the basis of these results, interface engineering using ALD-ZrO₂-NLs is a promising approach for the fabrication of high-performance HfO₂-based ferroelectric devices.

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