Ferroelectric HfO₂-based materials for next-generation ferroelectric memories

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Ferroelectric random access memory (FeRAM) based on conventional ferroelectric perovskites, such as Pb(Zr,Ti)O₃ and SrBi₂Ta₂O₉, has encountered bottlenecks on memory density and cost, because those conventional perovskites suffer from various issues mainly including poor complementary metal-oxide-semiconductor (CMOS)-compatibility and limited scalability. Next-generation cost-efficient, high-density FeRAM shall therefore rely on a material revolution. Since the discovery of ferroelectricity in Si:HfO₂ thin films in 2011, HfO₂-based materials have aroused widespread interest in the field of FeRAM, because they are CMOS-compatible and can exhibit robust ferroelectricity even when the film thickness is scaled down to below 10 nm. A review on this new class of ferroelectric materials is therefore of great interest. In this paper, the most appealing topics about ferroelectric HfO₂-based materials including origins of ferroelectricity, advantageous material properties, and current and potential applications in FeRAM, are briefly reviewed.

Keywords: HfO₂; nonvolatile memory; FeRAM; ferroelectric; thin film; orthorhombic phase.

1. Introduction

Ferroelectric materials exhibit bi-stable polarization states $\pm P_r$, which can be used to store binary information of “0” and “1” in a nonvolatile fashion. The switching between “0” and “1” (i.e., two polarization states) is driven by an electric field and therefore causes ultralow energy dissipation. This great advantage makes ferroelectric random access memory (FeRAM) very competitive among various emerging current-driven nonvolatile memory technologies, such as NOR-FLASH memory, spin torque transfer magnetic RAM (STT-MRAM), resistive RAM (RRAM), and phase change RAM (PCRAM). Although FeRAM has been extensively investigated for more than 60 years,¹ it has still been restricted to a tiny niche in the memory market. This is because the state-of-the-art FeRAM is based on perovskite ferroelectrics, such as Pb(Zr,Ti)O₃ (PZT)² and SrBi₂Ta₂O₉ (SBT),³ which suffer from the issues including poor complementary metal-oxide-semiconductor (CMOS)-compatibility and limited scalability. The CMOS-compatibility issue complicates the integration of perovskite ferroelectrics and related electrodes into the CMOS platform, which adds to the cost of manufacturing and processing. Meanwhile, the scalability issue limits the size of the memory cell and thus leads to low memory density. Solutions to these issues are therefore of great importance to the future development of FeRAM, and shall rely on a material revolution.

The first discovery of ferroelectricity in Si-doped HfO₂ ultrathin films in the year of 2011⁴ has brought opportunities to overcoming the aforementioned issues of conventional

perovskites. HfO₂, representing a class of simple binary oxides, has already been established as high-*k* dielectric materials in the CMOS technology. Moreover, the ferroelectricity in HfO₂ can be preserved even when the film thickness is reduced to only ~ 10 nm⁴; thus endowing HfO₂ superior scalability for high-density FeRAM. As simultaneously being CMOS-compatible and highly scalable, HfO₂ and its analogous ferroelectric materials^{5,6} have quickly become a hot research topic in both academic and industry communities for their great potential in FeRAM applications. More recently, based on ferroelectric HfO₂, both the one-transistor (1T) FeRAM at the 28 nm node⁷ and the one-transistor-one-capacitor (1T-1C) FeRAM with 3D deep trench capacitors⁸ have been successfully developed, which will undoubtedly boost the research and development of HfO₂-based materials and devices.

Because there have been several excellent review papers related to this topic published elsewhere,^{9–12} this paper will not aim to be exhaustive and will mainly focus on origins of ferroelectricity in HfO₂-based materials, their advantageous properties, and current and future applications of these materials in FeRAM.

2. Origins of Ferroelectricity in HfO₂-based Materials

HfO₂ in the bulk form exhibits the most stable phase of monoclinic P2₁/c (m-phase) at room temperature and under atmospheric pressure. As temperature increases to $\sim 1700^\circ\text{C}$ and further to $\sim 2600^\circ\text{C}$, HfO₂ will undergo phase transition

from monoclinic to tetragonal $P4_2/nmc$ (t-phase) and then to cubic $Fm3m$ (c-phase).¹³ On the other hand, applying hydrostatic compressive pressure to the m-phase of HfO_2 will induce the formation of orthorhombic phases (o-phase), such as $Pbca$ at 4 GPa and $Pnma$ at 14.5 GPa.^{14–16} All the above polymorphs of HfO_2 have inversion symmetry and hence their relationship to ferroelectricity can be ruled out. However, surprisingly, ferroelectricity was discovered in Si-doped HfO_2 thin films with the thickness of ~ 10 nm and with less than 4% Si dopant.⁴ Böschke *et al.*⁴ attributed the observed ferroelectricity to the formation of a polar orthorhombic phase, $Pca2_1$ (Fig. 1). This o-phase was first identified in Mg-doped ZrO_2 ceramics by Kisi and Howard⁷ using neutron powder diffraction. (Note: ZrO_2 is structurally and chemically similar to HfO_2 .) In a later theoretical work, Huan *et al.*¹⁸ proposed that two orthorhombic phases with polar space groups of $Pca2_1$ and $Pmn2_1$ were possible to be the ferroelectric phases of HfO_2 , because their calculations showed that both $Pca2_1$ and $Pmn2_1$ phases had low free energies and small energy barriers for polarization switching. More recently, Sang *et al.*¹⁹ provided supportive evidence for the existence of the $Pca2_1$ phase as the structural origin of ferroelectricity in Gd: HfO_2 thin films using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) in combination with position averaged convergent beam electron diffraction (PACBED). They

observed that Hf atom columns projected along [100], [010], [001] and [110] zone axes were consistent with those expected for the $Pca2_1$ phase (Figs. 2(a) and 2(b)). The other polar phase $Pmn2_1$ has significantly different projections of Hf atom columns and thus it can be excluded from the possible phases of HfO_2 ; however, the existence of other non-polar orthorhombic phases, such as $Pbcm$ and $Pbca$, still could not be determined because they exhibit very similar projections of Hf atom columns as the $Pca2_1$ phase. To further distinguish the polar $Pca2_1$ phase from the nonpolar $Pbcm$ and $Pbca$ phases, Sang *et al.*¹⁹ examined the symmetry of the HfO_2 phase being investigated using the PACBED technique. As shown in Fig. 2(c), the observed PACBED pattern lacks the mirror plane perpendicular to the [001] axis, which is a polar feature and is in near-perfect agreement with the simulated pattern of the $Pca2_1$ phase. The absence of the mirror plane in the PACBED pattern also denies the existence of centrosymmetric $Pbcm$ and $Pbca$ phases. Up to this point, it has been concluded that the ferroelectricity in HfO_2 -based thin films stems from the polar orthorhombic $Pca2_1$ phase.

One remaining question is how this o-phase ($Pca2_1$) is formed in HfO_2 -based thin films, especially allowing for the existence of various competitive phases, like t-, m-, and c-phases. It has been believed that the o-phase is transformed from the t-phase because of their structure similarities.²⁰ For example, the lattice parameters of the undoped HfO_2 o-phase are $a = 5.30$ Å, $b = 5.10$ Å, $c = 5.11$ Å (note: the direction of P_r is along the c -axis),²¹ while those of the t-phase are $a = b = 5.14$, $c = 5.25$ Å.²² Thus, the a -axis of the o-phase can be obtained by elongating the c -axis of the t-phase, while the b - and c -axes of the o-phase can be obtained by shrinking and differing the a - and b -axes of the t-phase. In this connection, anisotropic stresses are required for the phase transition from tetragonal to orthorhombic, i.e., a compressive stress within the aob plane and a tensile stress along the c -axis exerted on the t-phase. There are many factors reported hitherto to be responsible for causing the anisotropic stresses and thus stabilizing the ferroelectric o-phase during the film growth, such as doping,^{4,5,23–35} surface energy effect,^{36–38} island coalescence,³⁹ thermal expansion mismatch,¹⁷ capping layer effect,^{4,38} and formation of oxygen vacancies.⁴⁰ The following of this section will discuss each of these factors in order.

(i) *Doping.* Besides the initially reported Si, many other dopants, including Zr,^{5,26,27} Y,^{28–31} Al,³² Gd,³³ Sr,³⁴ and La³⁵ have also been reported to induce the ferroelectricity in HfO_2 -based thin films. Doping is able to stabilize the o-phase of HfO_2 with appropriate dopant concentrations, because dopants with ionic sizes different from that of Hf can significantly modify the metal–oxygen bonding and further change the relative stabilities of various HfO_2 phases.⁴¹ For example, without doping, the m-phase HfO_2 is the most stable one; however, in the presence of dopants, t-phase and

Fig. 1. Polymorphs of HfO_2 : (a) tetragonal $P4_2/nmc$; orthorhombic $Pca2_1$ with (b) polarization up and (c) polarization down. The displacements of oxygen atoms in the $Pca2_1$ structures are clearly seen in (b) and (c). Reproduced from Ref. 4, Copyright 2011, AIP Publishing LLC.

Fig. 2. (a) Theoretical crystal structure of $Pca2_1$ projected along four major zone axes: $[100]$, $[010]$, $[001]$, and $[110]$. (b) Experimental HAADF-STEM images acquired from four different grains superimposed with Hf atom columns projected along the four major zone axes. (c) Experimental and (d) simulated PACBED patterns of HfO_2 projected along the $[110]$ direction. The white arrows in (c) and (d) indicate the polar $[001]$ axis. Reproduced from Ref. 19, Copyright 2015, AIP Publishing LLC.

c-phase can become stable. According to the crystal radii,^{42,43a} the dopant ions are classified into two classes: (i) Si^{4+} (54 pm), Al^{3+} (67.5 pm), and Zr^{4+} (86 pm), whose crystal radii are smaller than or similar to that of Hf^{4+} (85 pm); and (ii) Y^{3+} (104 pm), Gd^{3+} (108 pm), La^{3+} (117 pm), and Sr^{2+} (132 pm), which have larger crystal radii than Hf^{4+} . The Class I dopant ions tend to stabilize the t-phase, while the Class II dopant ions first favor the t-phase and eventually stabilize the c-phase as the dopant concentration increases.⁴² The suppression of m-phase and the

preference of t/c-phases caused by doping are the prerequisites for the formation of the o-phase. For each of the above dopants, the o-phase always exists in a transition region between the m-phase and the t/c-phase in the phase-dopant concentration diagram; and within that region, the ferroelectricity can be induced.⁴⁴ The ferroelectric properties measured for various dopants are summarized in Fig. 3. Because the ionic size and the chemical valence of Zr are almost the same as those of Hf, the $Hf_{1-x}Zr_xO_2$ solid solution can be formed over the entire range of x . Ferroelectricity

^a“Crystal radii” are one widely-accepted set of ionic radii published by Shannon *et al.*⁴¹ Here, a simple consideration of ionic radii is adopted, while the covalent character of bonding is neglected.

Fig. 3. (a) Polarization (P) and dielectric constant (P_r) as a function of electric field measured for $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ thin films with x ranging from 0 to 1. Reproduced from Ref. 5, Copyright 2012, American Chemical Society. (b) Contour plot of remnant polarization (P_r) as a function of crystal radius and dopant content. Reproduced from Ref. 45, Copyright 2014, The Japan Society of Applied Physics.

emerges at $x = 0.3$ and becomes most distinct at $x = 0.5$, while antiferroelectricity turns up when x is larger than 0.5 (Fig. 3(a)). Other dopants have their respective ranges of concentrations where the ferroelectric polarizations become measurable (Fig. 3(b)). All the dopants have induced appreciable ferroelectricity with the P_r of 10–30 $\mu\text{C}/\text{cm}^2$ and the coercive field (E_c) of 1–2 MV/cm at the optimal dopant concentrations, except the dopant of La which could induce a P_r as high as 45 $\mu\text{C}/\text{cm}^2$. Note that for all doped HfO₂ thin films, the measured polarizations were smaller than the theoretical value of the o-phase ($P_r = 50\text{--}60 \mu\text{C}/\text{cm}^2$),¹² because all the films under investigation had mixed phases rather than the pure ferroelectric o-phase. We also note that besides the nominal dopant concentrations, the real dopant distributions could also significantly influence the ferroelectric properties of the doped HfO₂ thin films, through either modifying the local phase composition (ferroelectric/antiferroelectric) or causing the local defect accumulation pinning the domain wall motions.⁴⁴

(ii) *Surface energy effect.* Surface energy effect often manifests itself by creating unique structures and properties of small-size crystals which can be quite different from those of bulk materials. The surface energy effect has been well known in playing a great role in the phase formation in HfO₂ and ZrO₂ nanoscale thin films. For example, the t-phase of HfO₂ can become more stable than the m-phase when the grain size is below $\sim 4 \text{ nm}$ ($\sim 32 \text{ nm}$ for ZrO₂).^{46,47} The surface energy effect also contributes to the stabilization of o-phase, in accordance with very recent computational results.³⁷ In their work, Materlik *et al.*³⁷ built the Helmholtz free energy model, which contain both an *ab initio* computed part for total energy and entropy, and a phenomenological part for the surface energy. By comparing the Helmholtz free energies of various HfO₂ (and Hf_{0.5}Zr_{0.5}O₂) phases, it was found that the o-phase became the lowest-in-energy for HfO₂ when the grain size was 3–5 nm (8–16 nm for Hf_{0.5}Zr_{0.5}O₂).³⁷ On the other hand, experimentally, Yurchuk *et al.*³⁶ first reported that in Si: HfO₂ thin films, as the film

thickness increased from 9 nm to 27 nm, the P_r dropped from $24 \mu\text{C}/\text{cm}^2$ to $3.5 \mu\text{C}/\text{cm}^2$. The similar inverse relation between P_r and film thickness was also found in undoped HfO_2 ³⁸ and $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ solid solution films.³⁹ The reason for the reduction of P_r with film thickness is well understood because as film thickness increases, the surface energy effect is weakened and thus the portion of the nonferroelectric m-phase will increase and gradually dominate over that of the ferroelectric o-phase. To avoid the coarsening of grains as film thickness increases, Kim *et al.*⁴⁸ applied an Al_2O_3 interlayer to interrupt the continual growth of $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ thin films. Within the $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2/\text{Al}_2\text{O}_3/\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ multilayer thin films, the thickness of each $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ layer was kept as small as ~ 10 nm and therefore, the grain size was properly controlled. Using this method, a satisfactory $2P_r$ value of $\sim 22.7 \mu\text{C}/\text{cm}^2$ was retained although the total film thickness was increased up to 40 nm. More recently, Starschich *et al.*³⁰ reported in their Y:HfO₂ films prepared by chemical solution deposition (CSD) method, there was no decay of P_r even when the total film thicknesses was increased to 70 nm. Although the origin of the undiminished P_r with increasing thickness has not been completely understood, it might be due to the step-by-step process of coating-annealing-crystallization in the CSD method, which could produce the Y:HfO₂ layer as thin as ~ 7 nm in each step. While the grain size in each layer remained small, the total thickness could be additive without sacrificing the ferroelectricity. Note that this first time report of robust ferroelectricity in relatively thick films has extended the applications of HfO₂-based materials to piezoelectric sensors and actuators.

(iii) *Island coalescence.* In the Volmer–Weber-type (island) growth mode, stress could be formed during the island coalescence (also known as island zipping).⁴⁹ Park *et al.*³⁹ first proposed this coalescence (zipping) stress as the driving force to stabilize the ferroelectric o-phase. In their $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ polycrystalline films deposited on TiN/Si substrates, ferroelectricity emerged only when the in-plane tensile strain surpassed a critical value of $\sim 1.5\%$ (this tensile strain corresponded to a tensile stress of ~ 4.7 GPa). Therefore, the formation of ferroelectric o-phase was associated with the in-plane tensile stress. In terms of the nature of the stress, several possible stresses were considered and compared. According to their estimations, surface and thermal stresses were as small as ~ 0.1 and <2 GPa, respectively, while the coalescence stress could reach as large as ~ 30 GPa. The coalescence stress was therefore regarded as the most plausible stress to promote the t–o phase transition and stabilize the o-phase.

(iv) *Thermal expansion mismatch.* This mechanism was proposed to explain the early observation of o-phase in Mg partially stabilized ZrO₂ (Mg–PSZ) ceramics.¹⁷ As reported by Kisi,⁵⁰ the Mg–PSZ sample exhibited t-phase lenticular precipitates which were surrounded by a c-phase matrix. Upon cooling from 1373 to 80 K, a large tensile stress

(~ 760 MPa) along the *c*-axis and small compressive stresses (~ 50 MPa) along *a*- and *b*-axes were developed, due to the different coefficients of thermal expansion (CTEs) of t- and c-phases along different axes. (CTEs of the t-phase: $1.43 \times 10^{-5} \text{ K}^{-1}$ along *c*-axis and $1.01 \times 10^{-5} \text{ K}^{-1}$ along *a*- and *b*-axes; CTEs of the c-phase: $1.11 \times 10^{-5} \text{ K}^{-1}$ along *a*-, *b*-, and *c*-axes). These anisotropic stresses caused by the thermal expansion mismatch were therefore exactly what the t–o phase transition needed, and they successfully induced the formation of o-phase in Mg–PSZ ceramics, although they seemed to be smaller than the theoretical stresses required for the t–o phase transition (e.g., 3.6 GPa tensile stress along the *c*-axis). Also because these thermal expansion induced stresses are small in magnitude, they have not been often considered in recently reported HfO₂/ZrO₂-based thin films.³⁷

(v) *Capping layer effect.* In their first paper reporting the discovery of ferroelectricity in HfO₂-based materials, Böschke *et al.*⁴ stressed the important role of top capping electrodes in stabilizing the ferroelectric o-phase. They prepared two different 3% Si-doped HfO₂ samples without and with the TiN capping layer, i.e., one sample was crystallized without depositing a TiN capping layer beforehand while in the other sample, a TiN top layer was used to encapsulate the amorphous Si:HfO₂ film prior to annealing the film at 1000°C. As shown in Fig. 4, distinct differences in crystal structures and dielectric behavior can be seen in samples without and with capping. The XRD pattern of the sample without capping shows a good match to the m-phase whereas that of the sample with capping shows strong diffraction peaks from the o-phase rather than the m-phase (Fig. 4(a)). Moreover, the capacitance–voltage (*C*–*V*) behavior of the sample without capping is almost linear over the whole voltage range whereas that of the sample with capping exhibits a peak near the coercive voltage, which is a typical feature of ferroelectricity (Fig. 4(b)). These experimental results indicate that the capping layer induces the crystallization of o-phase and however without capping the phase transition toward the m-phase occurs. Böschke *et al.* in Ref. 4, and Polakowski and Müller in Ref. 38 further proposed that the function of the capping layer was a mechanical confinement, which prevented the volume expansion and shearing of the HfO₂ unit cell, and thus inhibited the formation of the m-phase. Another different function of the capping layer was also suggested, i.e., preventing the ion migration on the film surface during annealing to suppress the grain coarsening as well as the accompanying m-phase formation. Although the working mechanisms of the capping layer have not been clearly unraveled, most works have adopted the method of encapsulating HfO₂-based amorphous thin films with top electrodes prior to annealing. Besides the commonly used TiN, various capping layer materials have been studied, such as Pt,⁵¹ RuO₂,⁵² TaN,⁴⁰ and Ir/IrO_x.^{53,54} In particular, using Ir/IrO_x as electrodes has successfully solved the long-standing

Fig. 4. (a) Grazing incidence X-ray diffraction patterns of two different 3% Si-doped HfO₂ samples without and with the TiN capping layer. C–V characteristics of these two samples (b) without and (c) with TiN layer. Reproduced from Ref. 4, Copyright 2011, AIP Publishing LLC.

fatigue issue of PZT⁵⁵ and is therefore of great interest to be applied to HfO₂-based devices. However, in the case of Si: HfO₂ thin films, the Ir capped capacitor exhibited 13–14% lower P_r than the TiN capped capacitor, which was attributed to different thermal expansion coefficients and the potential scavenging effect of TiN.⁵³ Also note that there were some exceptional examples, such as Hf_{0.5}Zr_{0.5}O₂ films³⁹ and Y: HfO₂ films,³⁰ where no capping layers were used before the films were crystallized but the ferroelectricity was almost unaffected. These results suggest that the role of the capping layer is positive but not critical in inducing the formation of ferroelectric o-phase.

(vi) *Formation of oxygen vacancies.* In HfO₂-based thin films, the oxygen vacancies are formed due to the oxidation of TiN during the growth of HfO₂ and also due to the aliovalent doping of HfO₂. Oxygen vacancies can influence the stabilities of various HfO₂ phases. In the calculations performed by Lee *et al.*,⁴¹ metastable t- and c-phases could be stabilized over the m-phase in the presence of oxygen vacancies. The similar computational result of improved stability induced by oxygen vacancies was also reported for the o-phase.⁴¹ Experimentally, a larger concentration of oxygen vacancies was observed

in the Gd:HfO₂ film grown on the TaN bottom electrode compared with that grown on the TiN bottom electrode.⁴⁰ As a result, in the Gd:HfO₂/TaN film, the fraction of the o-phase became larger and an enhanced P_r of up to 35 $\mu\text{C}/\text{cm}^2$ was measured. It is noteworthy that despite the positive effect of stabilizing the desired o-phase, the oxygen vacancies may also have some negative effects. For example, their accumulation near the bottom electrode/film interface causes the band bending and thus develops a built-in field, which suppresses the nucleation of domains with the opposite polarity.²⁵

To summarize this section, the structural origin of ferroelectricity in HfO₂-based thin films is due to the formation of a polar orthorhombic $Pca2_1$ phase. The real mechanism how this o-phase is stabilized over other competitive phases in HfO₂-based thin films, however, has not been fully elucidated and many plausible factors which can induce the formation of the o-phase have been reported. Nevertheless, no matter which of these factors lead to the ferroelectricity in HfO₂, HfO₂ can become ferroelectric. The emerging ferroelectricity of HfO₂ together with its many other advantageous material properties, which will be described in the following section, makes HfO₂ very promising for the FeRAM applications.

3. Advantageous Properties of Ferroelectric HfO₂-based Materials

HfO₂-based materials show tremendous potential to replace the conventional perovskites for the FeRAM applications, because of the emerging and unique ferroelectricity (preserved P_r in ultrathin films and extremely large E_c) plus many other superior properties related to the applicability in the semiconductor technology. As summarized in Table 1, HfO₂ exhibits a satisfactory P_r (1–45 $\mu\text{C}/\text{cm}^2$) and more importantly, the P_r can be retained even when the film thickness is scaled down to 5 nm.⁹ This is one of the major advantages when compared to SBT and PZT, whose P_r can be preserved only when the film thickness is above several tens of nanometers. This capability of maintaining P_r at such a small thickness is due to the stabilized HfO₂ o-phase in ultrathin films. In addition, this capability is also associated with the low leakage current and high breakdown field (E_{BD}) of HfO₂-based thin films. In HfO₂ there is strong Hf–O bonding, together with a large bandgap (>5 eV) and a high conduction band offset to nitride-based electrodes,¹² all of which contribute to the low leakage current and high E_{BD} . Table 1 also indicates an extraordinarily high E_c (1–2 MV/cm) of HfO₂, which is one order of magnitude larger than those of conventional perovskites. Such a giant E_c prevents the depolarization effect which often occurs in ultrathin films and therefore is beneficial to the polarization stability. Moreover, enhancing E_c can effectively compensate the loss of memory window (MW) caused by reducing the film thickness (note: $\text{MW} \approx 2E_c t_f$, where t_f is the film thickness; MW is one key parameter in 1T FeRAM). The large E_c being closer to E_{BD} (Table 1),

Table 1. Comparison of material properties between HfO₂ and conventional perovskites. Reproduced from Ref. 9, Copyright 2014, The Electrochemical Society.

	SrBi ₂ Ta ₂ O ₉ (SBT)	Pb(Zr _x Ti _{1-x})O ₃ (PZT)	FE-HfO ₂
Film thickness	> 25 nm	> 70 nm	5–30 nm
Annealing temp.	> 750°C	> 600°C	450–1000°C
P_r	< 10 $\mu\text{C}/\text{cm}^2$	20–40 $\mu\text{C}/\text{cm}^2$	1–45 $\mu\text{C}/\text{cm}^2$
E_c	10–100 kV/cm	~ 50 kV/cm	1–2 MV/cm
E_{BD}	~ 2 MV/cm	0.5–2 MV/cm	4–8 MV/cm
E_c/E_{BD}	0.5–5%	2.5–10%	12.5–50%
Dielectric constant	150–200	~ 1300	~ 30
ALD capacity	Limited	Limited	Mature
CMOS compatibility	Bi and O ₂ diffusion	Pb and O ₂ diffusion	Stable
BEOL compatibility	H ₂ damage	H ₂ damage	Stable

however, may also cause a switching endurance issue because the film is more vulnerable to breakdown during the field cycling. Then, one can also see from Table 1 that the dielectric constant of HfO₂ is relatively low. A low dielectric constant reduces the nonswitching capacitive current and therewith improves the nonswitching to switching polarization sensing margin. In terms of the practical applicability, HfO₂ is highly compatible to the standard CMOS technology, which is cost-efficient compared with conventional perovskites. The matured atomic layer deposition (ALD) technique enables the fabrication of 3D nanostructures of HfO₂, which allows for an area enhancement to the third dimension.

With these above superior properties, HfO₂ could potentially replace the conventional perovskites for FeRAM applications. The recent development of HfO₂-based 1T-1C and 1T FeRAM may be viewed as a signal for the coming revolution in FeRAM.

4. Applications of Ferroelectric HfO₂-based Materials in FeRAM

As demonstrated in the pioneering works done by the Müller’s group, ferroelectric HfO₂ has been successfully implemented into two types of FeRAM with different architectures, i.e., 1T-1C and 1T.^{7,8} The 1T-1C architecture in FeRAM is very similar in construction to that in the DRAM, where the major difference is that FeRAM uses ferroelectrics while DRAM uses linear dielectrics for their respective capacitor parts. The 1T-1C FeRAM based on conventional perovskites has been commercialized nowadays and however stagnated at a low memory density level of 128 MB/cm²,⁵⁶ because conventional perovskites have thickness scaling issues and they also lack feasible deposition techniques for 3D nanostructures (Fig. 5(a)). On the contrary, with excellent thickness scalability and ALD-feasibility, HfO₂ is suitable for fabrication of 3D trench and stack capacitors to achieve significant area enhancement (Fig. 5(c)) for the 1T-1C FeRAM. On the other hand, the 1T FeRAM, namely ferroelectric field effect transistor (FeFET), utilizing ferroelectrics as the gate materials, is very promising in terms of a smaller cell size compared to the 1T-1C architecture and the non-destructive reading. However, the 1T FeRAM based on

Fig. 5. Schematics of the state-of-the-art perovskites-based FeRAM: (a, Ref. [A] or 2) 1T-1C, and (b, Ref. [B] or 3) 1T, compared to corresponding ferroelectric HfO₂-based FeRAM: (c, Ref. [C] or 8) 1T-1C and (d, Ref. [D] or 7) 1T. Reproduced from Ref. 10, Copyright 2014, IEEE.

conventional perovskites has not been commercialized yet due to the poor CMOS-compatibility of conventional perovskites. Additionally, the scaling issue is still there because conventional perovskites with low coercive fields and high dielectric constants require the ferroelectric layers to be thick (above 100 nm) in order to achieve a reasonable MW (Fig. 5(b)). As HfO_2 shows unique scaling advantages and also good compatibility with Si as a gate material, it has been successfully used to fabricate the world's most aggressively scaled 1T FeRAM (Fig. 5(d)). The remainder of this section will describe the key device performance of both 1T-1C and 1T FeRAM based on HfO_2 , according to the reports from Müller *et al.*^{7,8}

3D trench capacitors based on Al:HfO_2 with the number of trenches ranging from 1000 to 100,000 and an aspect ratio of 13:1 were fabricated for the 1T-1C FeRAM (Fig. 5(c)). As can be seen from Fig. 6(a), the measured P_r increases from $15 \mu\text{C}/\text{cm}^2$ to $152 \mu\text{C}/\text{cm}^2$ monotonically as the number of trenches increases. The calculated area gain factor reaches as large as 11.12 for the 100,000 trench array. Figure 6(b) shows the area normalized P - E loops of different trench arrays in comparison to the planar capacitor. There is a loss of normalized P_r with the increasing trench number; however, the loss is not substantial, only 11% for the 100,000 trench array. The cycling endurance measurements were conducted for 100,000 trench array, and the results are summarized in

Fig. 6. Device performance of 3D trench capacitors based on Al:HfO_2 : (a) P - E loops measured for different trench arrays (top) and the calculated area gain factor as a function of the number of trenches. (b) P - E loops (normalized to the real capacitor area) of different trench arrays (top) and the relative polarization loss as a function of the number of trenches. (c) Endurance characteristics of the 100,000 trench array under different applied fields. Reproduced from Ref. 8, Copyright 2014, IEEE.

Fig. 7. Device performance of a MFIS-FET with a TiN/Si:HfO₂/SiO₂/Si gate stack: (a) I_d - V_g hysteresis and an inset showing the P - E loop; (b) retention; and (c) endurance characteristics. Reproduced from Ref. 7, Copyright 2012, IEEE.

Fig. 6(c). The highest endurance under the applied field of 2.5 MV/cm is 2×10^9 cycles (note: the conventional perovskites can withstand 10^{12} endurance cycles⁵⁷). Although lowering the applied field to 2 MV/cm can increase the endurance to above 10^{10} cycles, the switching shows sub-loop behavior and thus a strong polarization fatigue effect is observed. Enhancing the applied field leads to more saturated switching and however causes dielectric breakdown more rapidly. The above results suggest that HfO₂ exhibits excellent 3D-capability and scalability, which is very promising to scale down the lateral size of the capacitor in the 1T-1C FeRAM and therefore increase the memory density. However, the endurance of HfO₂-based 3D trench capacitors needs to be further improved to compete against the conventional perovskites.

Metal-ferroelectric-insulator-semiconductor FETs (MFIS-FETs) with a TiN/Si:HfO₂/SiO₂/Si gate stack were fabricated with the gate length of only ~ 28 nm. The drain current-gate voltage (I_d - V_g) characteristics were measured after applying a 5 V, 100 ns erase and a -5 V, 100 ns program pulse. As shown in Fig. 7(a), the distinct I_d - V_g hysteresis is observed and a MW of ~ 0.8 V is revealed. In the retention test, a residual MW of ~ 0.6 V can be retained after 10 years in accordance with linear extrapolation (Fig. 7(b)). The endurance is, however, limited to $\sim 10^4$ cycles due to the charge injection issue (Fig. 7(c)), which is relatively low and narrows the application fields of Si:HfO₂-based FeFETs. In brief, highly scaled 1T FeRAM based on Si:HfO₂ at the 28 nm node has been successfully fabricated and it has shown a satisfactory MW, fast switching, good retention, and relatively low endurance. The endurance of this type of FeRAM could be improved to 10^{12} cycles, as has recently been reported by Cheng and Chin⁵⁸ for Hf_{0.5}Zr_{0.5}O₂-based FeFETs. However, the voltages used for programming and erasing were low, resulting in a sub-loop operation and a relatively low retention time (an I_{on}/I_{off} ratio of 10^3 could be retained after 10 s).⁵⁸

5. Summary

In summary, HfO₂-based materials have emerged as a new class of ferroelectric materials which are very promising for

the next-generation cost-efficient, high-density FeRAM. The ferroelectricity in HfO₂-based materials originates from a polar orthorhombic *Pca*2₁ phase, and there have been a variety of factors which can induce the formation of this o-phase. The ferroelectric properties of HfO₂-based materials are unique, including an exceptionally high E_c (1–2 MV/cm) and a satisfactory P_r (1–45 $\mu\text{C}/\text{cm}^2$) even at an ultra-small film thickness (~ 10 nm). They therefore show several advantages over the conventional ferroelectric perovskites for the FeRAM applications, such as CMOS-compatibility, scalability, and 3D-capability. In terms of FeRAM applications, both 1T-1C FeRAM with 3D trench capacitors and 1T FeRAM at the 28 nm node based on ferroelectric HfO₂ have been successfully developed and they have both demonstrated good device performance. Future research focusing on the following directions may yield fruitful results: (i) developing polycrystalline or epitaxial thin films with pure and stabilized o-phase for both fundamental research on this novel phase and better device performance due to enhanced ferroelectric properties. (ii) Improving the endurance properties of HfO₂-based FeRAM by engineering HfO₂-based materials and/or electrodes for higher breakdown strength, as the endurance of current HfO₂-based devices is limited by the dielectric breakdown issue. (iii) Properly tailoring the trade-off between endurance and retention to meet the requirements of different memory applications.

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