REVIEW ARTICLE
Min Hyuk Park, Uwe Schroeder, Cheol Seong Hwang et al.
Review of defect chemistry in fluorite-structure ferroelectrics for future electronic devices
Review of defect chemistry in fluorite-structure ferroelectrics for future electronic devices

Min Hyuk Park, Dong Hyun Lee, Kun Yang, Ju-Yong Park, Geun Taek Yu, Hyeon Woo Park, Monica Materano, Terence Mittmann, Patrick D. Lomenzo, Thomas Mikolajick, Uwe Schroeder and Cheol Seong Hwang

Ferroelectricity in fluorite-structure oxides, such as (doped) HfO₂ and ZrO₂, and their solid solution, nanolaminates, and superlattices has attracted increasing interest for future memory devices. The scalability of film thickness down to only several nm and the availability of matured deposition techniques render these materials highly practical for future high-density memory applications. Significant effort is being made in the community to identify the possible reasons for establishing solid physical backgrounds for the emergence of the (unexpected) ferroelectricity in these materials. Nonetheless, several technical obstacles must be overcome before adopting ferroelectric HfO₂ for practical device applications. Among them, understanding the role of various forms of defects in ferroelectric phase formation and evolution of the device performance is crucial. The forms of defects include point defects such as oxygen vacancies, extrinsic defects such as residual carbon, nitrogen, and hydrogen, and two-dimensional defects such as an interfacial layer at the electrode interface and grain boundaries. Numerous previous studies on non-ferroelectric HfO₂ or non-fluorite-structure ferroelectrics could form the foundation for the understanding of such thematics. In this review, the influences of various kinds of defects on the formation mechanism of various polymorphisms, and the accompanying ferroelectric and electrical properties are comprehensively studied based on previous literature. This review is expected to contribute to a better understanding of these emerging ferroelectric materials and to provide the community with new insights motivated by the previous studies on non-ferroelectric HfO₂ and non-fluorite-structure ferroelectrics.

Introduction

Ferroelectricity in fluorite-structure oxides, such as (doped) HfO₂ and ZrO₂, and their solid solution, nanolaminates, and superlattices has attracted increasing interest since the original report by Boescke et al. in 2011. In contrast to the conventional ferroelectrics based on perovskite or layered perovskite structure, the fluorite-structure ferroelectrics can be deposited even on complicated three-dimensional nanostructures due to mature deposition techniques, such as atomic layer deposition (ALD). Moreover, fluorite-structure ferroelectrics are compatible with complementary metal-oxide-semiconductor (CMOS) systems. It is particularly noteworthy that HfO₂ and ZrO₂ are currently utilized for the mass production of state-of-the-art semiconductor devices as a gate insulator in metal-oxide-semiconductor field-effect-transistors (MOSFETs) and as a dielectric layer in capacitors of dynamic random-access-memories (DRAMs), respectively. Therefore, the fluorite-structure ferroelectrics are considered highly promising as emerging ferroelectric materials for next-generation memory devices, such as ferroelectric random access memories (FeRAMs), ferroelectric field-effect-transistors (FeFETs), ferroelectric tunnel junctions (FTJs), negative capacitance field-effect-transistors (NCFETs), and various energy-related applications.

Despite the short history of ferroelectric HfO₂, FeFETs with channel length shorter than 30 nm were already fabricated and characterized. In 2018, a fully depleted silicon-on-insulator (FDSOI) device was also reported by Duenkel and coworkers. Besides the non-volatile memory for storage or storage class memory, logic is another category where FeFETs can be utilized, as reviewed in a recent book chapter.
also suggested that FeFETs can be used as synaptic devices. For instance, Kim and Lee\textsuperscript{18} reported the analog synaptic behaviour of FeFETs with an indium gallium zinc oxide (IGZO) channel. Another interesting device which can incorporate HfO\textsubscript{2} and ZrO\textsubscript{2} is the FTJ.\textsuperscript{19–21} Fujii \textit{et al.} first experimentally demonstrated the self-rectifying FTJ with ferroelectric Si-doped HfO\textsubscript{2} with top and bottom TiN electrodes.\textsuperscript{19} Goh and Jeon\textsuperscript{20} comparatively studied FTJs with various bottom electrodes/substrates, including TiN, Si, SiGe, and Ge, and top TiN electrodes. They suggested that the asymmetric TiN/Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2}/Ge-stack FTJ could meet the requirement of 10 year retention and 10\textsuperscript{7} cycle endurance. Chen \textit{et al.}\textsuperscript{21} reported a three-dimensional vertical array of low power (~1.8 pJ per spike) Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} based FTJs with synaptic behavior. Thus, both FeFET and FTJ device architectures have seen demonstrable progress in both feasibility and performance evaluation with the emergence of ferroelectric hafnia-zirconia oxides.

Although there have been numerous studies on ferroelectricity in fluorite-structure oxides and electronic devices utilizing them, many crucial aspects of fluorite-structure ferroelectrics have yet to be elucidated. Among them, the role of defects in fluorite-structure ferroelectrics needs specific attention. The defects can affect the fluorite-structure ferroelectrics in the following two main aspects: (1) polymorphism of fluorite-structure...
ferroelectrics by influencing the relative free energy of various crystalline phases and (2) electrical properties by inducing charge trap sites which affect the electrical conduction and reliability of the fabricated electronic devices.

The ferroelectricity in fluorite-structure oxides is associated with the formation of the non-centrosymmetric $Pca_2_1$ orthorhombic or rhombohedral phases. Boescke et al. suggested that the structural origin of the ferroelectricity would be the formation of the $Pca_2_1$ orthorhombic phase, and Sang et al. experimentally proved that the ferroelectric phase in Gd-doped HfO$_2$ thin films has an equivalent symmetry with that of the $Pca_2_1$ orthorhombic phase. In 2018, Wei et al. experimentally identified the ferroelectric rhombohedral phase (space group: $R3m$) in epitaxial Hf$_{0.5}$Zr$_{0.5}$O$_2$ thin films formed on a La$_{1-x}$Sr$_x$MnO$_3$/SrTiO$_3$ substrate, which was related to the epitaxial strain from the substrate.

The mechanism behind the ferroelectric phase formation has been intensively studied by several research groups, and thermodynamic stabilization due to various factors, such as doping, surface/interface/grain boundary energy effect, and strain, as well as a kinetic mechanism based on classical nucleation theory was suggested. The related studies were reviewed in a recent progress report and a book chapter.

For practical nanoscale electronic devices, defects can have critical effects on device performance. There have been many reports on the influence of various defects, including native defects such as oxygen vacancies, extrinsic defects like residual C, N, and H, and two-dimensional defects such as interfacial layers and grain boundaries, on the electrical performances of the ferroelectric thin films. This review provides a summary of these diverse reports, and establishes a framework for explaining the phase formation and the accompanying ferroelectric performances. Related previous studies on non-ferroelectric HfO$_2$ and ferroelectrics with non-fluorite-structure are also discussed for a more comprehensive understanding of this emerging ferroelectric system.

**Effect of doping**

**Overview**

Although ferroelectricity in undoped HfO$_2$ and ZrO$_2$ has been reported by several research groups, ferroelectricity in fluorite-structure oxides has been generally induced by doping since Boescke et al. first reported ferroelectricity in Si-doped HfO$_2$. Tables 1 and 2 summarize the ferroelectric properties of HfO$_2$ doped with various dopants and those of HfO$_2$-ZrO$_2$ solid solution systems. As can be seen in Tables 1 and 2, the ferroelectricity with a remanent polarization ($P_r$) of 5–40 $\mu$C cm$^{-2}$ and a coercive field ($E_c$) of 0.75–4 MV cm$^{-1}$ in fluoride-structure oxides could be experimentally confirmed for various dopants (e.g., Si, Al, Sr, La, Gd, Y, N, Sc) and deposition techniques (e.g., atomic layer deposition (ALD), physical vapor deposition (PVD), chemical solution deposition (CSD), pulsed laser deposition (PLD)).

Bulk phase diagrams of fluoride-structure oxides such as HfO$_2$ and ZrO$_2$ do not include the ferroelectric phase under any temperature and pressure conditions, suggesting that inducing ferroelectricity in bulk fluoride-structure oxides should be highly challenging. However, ferroelectricity in doped fluoride-structure oxide thin films has been robustly observed by many research groups, implying that the surfaces and interfaces play a key role in inducing a polar crystalline phase and the resulting ferroelectricity. It has been identified that appropriate doping was necessary to induce the ferroelectric phase in thin films.

In the following two subsections, current understanding of ferroelectric phase formation in fluoride-structure oxides accompanied by doping will be reviewed briefly from a thermodynamic and kinetic point of view.

**Thermodynamic effect**

The effect of doping on the free energy of various crystalline phases has been addressed in several works even before the
## Table 1 Experimental reports on ferroelectric doped HfO$_2$ films in the literature

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<tbody>
<tr>
<td>Polycrystalline Si:HfO$_2$</td>
<td>3.6 cat%</td>
<td>ALD</td>
<td>10</td>
<td>—</td>
<td>—/800°C</td>
<td>TIN/TiN</td>
<td>20.34</td>
<td>0.795</td>
<td>—</td>
<td>55</td>
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<tr>
<td>Polycrystalline Al:HfO$_2$</td>
<td>Hf:Al = 23:1 (ALD cycle ratio)</td>
<td>ALD</td>
<td>20</td>
<td>200</td>
<td>N$_2$/—</td>
<td>Ti/Pt/Si</td>
<td>20</td>
<td>2.05</td>
<td>10$^4$/3.5</td>
<td>56</td>
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<tr>
<td>Polycrystalline Sr:HfO$_2$</td>
<td>10 cat%</td>
<td>MOD (metal–organic decomposition)</td>
<td>49</td>
<td>150</td>
<td>O$_2$/700°C, 300 s</td>
<td>Au/Pt</td>
<td>13.3</td>
<td>0.75</td>
<td>—</td>
<td>57</td>
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<tr>
<td>Polycrystalline Sr:HfO$_2$</td>
<td>9.9 mol%</td>
<td>ALD</td>
<td>10</td>
<td>300</td>
<td>N$_2$/800°C, 20 s</td>
<td>TIN/TiN</td>
<td>23</td>
<td>2.0</td>
<td>—</td>
<td>58</td>
</tr>
<tr>
<td>Polycrystalline La:HfO$_2$</td>
<td>9.2 cat%</td>
<td>ALD</td>
<td>10</td>
<td>280</td>
<td>N$_2$/800°C, 20 s</td>
<td>TIN/TiN</td>
<td>27.7</td>
<td>1.2</td>
<td>10$^4$/7</td>
<td>59</td>
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<td>Polycrystalline Gd:HfO$_2$</td>
<td>2 mol%</td>
<td>ALD</td>
<td>10</td>
<td>300</td>
<td>1000°C, 1 s</td>
<td>TIN/TiN</td>
<td>12</td>
<td>1.75</td>
<td>—</td>
<td>60</td>
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<tr>
<td>Epitaxial YO$_{1.5}$–HfO$_2$</td>
<td>YO$_{1.5}$–HfO$_2$ = 0.07:0.93 (ALD cycle ratio)</td>
<td>PLD</td>
<td>14</td>
<td>450</td>
<td>—</td>
<td>ITO buffered (111)YINs substrates</td>
<td>10</td>
<td>2.0</td>
<td>—</td>
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<td>Epitaxial Si:HfO$_2$</td>
<td>3.4 cat%</td>
<td>ALD</td>
<td>9</td>
<td>300</td>
<td>N$_2$/1000°C, 1 s</td>
<td>TIN/TiN</td>
<td>24</td>
<td>—</td>
<td>—</td>
<td>62</td>
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<tr>
<td>Epitaxial Si:HfO$_2$</td>
<td>4.4 mol%</td>
<td>PLD</td>
<td>4.8</td>
<td>700</td>
<td>—</td>
<td>(Cr/Au)/0.7 mol% Nb:STO(110)$_p$</td>
<td>32</td>
<td>5</td>
<td>—</td>
<td>63</td>
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<tr>
<td>Epitaxial Al:HfO$_2$</td>
<td>4.8 mol%</td>
<td>ALD</td>
<td>16.2</td>
<td>300</td>
<td>N$_2$/1000°C, 1 s</td>
<td>TIN/TiN</td>
<td>5</td>
<td>1.0</td>
<td>—</td>
<td>64</td>
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<tr>
<td>Epitaxial La:HfO$_2$</td>
<td>10 cat%</td>
<td>ALD</td>
<td>12</td>
<td>280</td>
<td>N$_2$/800°C, 20 s</td>
<td>TIN/TiN</td>
<td>27.7</td>
<td>1.2</td>
<td>—</td>
<td>59</td>
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<tr>
<td>Polycrystalline Y:HfO$_2$</td>
<td>5.2 mol%</td>
<td>ALD</td>
<td>10</td>
<td>—</td>
<td>N$_2$/600°C, 20 s</td>
<td>TIN/TiN</td>
<td>24</td>
<td>1.2</td>
<td>—</td>
<td>65</td>
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<tr>
<td>Polycrystalline N:HfO$_2$</td>
<td>0.34 cat% N</td>
<td>Sputtering</td>
<td>28</td>
<td>—</td>
<td>N$_2$/600°C, 30 s</td>
<td>TIN/TiN</td>
<td>11.5</td>
<td>1.5–2</td>
<td>—</td>
<td>66</td>
</tr>
<tr>
<td>Polycrystalline Y:HfO$_2$</td>
<td>0.7 cat% Y</td>
<td>Sputtering</td>
<td>28</td>
<td>—</td>
<td>N$_2$/600°C, 30 s</td>
<td>Au/p-type Ge(111) substrate</td>
<td>10.5</td>
<td>1.5–2</td>
<td>—</td>
<td>66</td>
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<tr>
<td>Polycrystalline Sc:HfO$_2$</td>
<td>0.7 cat% Sc</td>
<td>Sputtering</td>
<td>28</td>
<td>—</td>
<td>N$_2$/600°C, 30 s</td>
<td>Au/p-type Ge(111) substrate</td>
<td>11.5</td>
<td>1.5–2</td>
<td>—</td>
<td>66</td>
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<tr>
<td>Polycrystalline N:HfO$_2$</td>
<td>0.34 cat% N</td>
<td>Sputtering</td>
<td>27</td>
<td>—</td>
<td>N$_2$/600°C, 30 s</td>
<td>Au/p-type Ge(111) substrate</td>
<td>11.5</td>
<td>1.5–2</td>
<td>—</td>
<td>66</td>
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<tr>
<td>Polycrystalline Ge:HfO$_2$</td>
<td>2.7 cat% Ge</td>
<td>Sputtering</td>
<td>27</td>
<td>—</td>
<td>N$_2$/600°C, 30 s</td>
<td>Au/p-type Ge(111) substrate</td>
<td>11.5</td>
<td>1.5–2</td>
<td>—</td>
<td>66</td>
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<tr>
<td>Polycrystalline Si:HfO$_2$</td>
<td>0.73 cat% Si</td>
<td>Sputtering</td>
<td>27</td>
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<td>N$_2$/600°C, 30 s</td>
<td>Au/p-type Ge(111) substrate</td>
<td>11.5</td>
<td>1.5–2</td>
<td>—</td>
<td>66</td>
</tr>
<tr>
<td>Polycrystalline Si:HfO$_2$</td>
<td>4.4 mol%</td>
<td>ALD</td>
<td>9</td>
<td>450</td>
<td>N$_2$/650–1000°C</td>
<td>TIN/TiN</td>
<td>20–21</td>
<td>1.0</td>
<td>10$^3$/3.5</td>
<td>69</td>
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<tr>
<td>Polycrystalline La:HfO$_2$</td>
<td>3–4 mol%</td>
<td>ALD</td>
<td>9</td>
<td>450</td>
<td>N$_2$/650–1000°C</td>
<td>TIN/TiN</td>
<td>40</td>
<td>1.2</td>
<td>—</td>
<td>70</td>
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<tr>
<td>Polycrystalline Si:HfO$_2$</td>
<td>5.2 mol%</td>
<td>CSD</td>
<td>45</td>
<td>—</td>
<td>Ar$_2$(1:1)/800°C, 90 s</td>
<td>Pt/Pt</td>
<td>20</td>
<td>1.4</td>
<td>—</td>
<td>72</td>
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<tr>
<td>Polycrystalline Si:HfO$_2$</td>
<td>~ 5.0 mol%</td>
<td>ALD</td>
<td>10</td>
<td>280</td>
<td>N$_2$/800°C, 20 s</td>
<td>TIN/TiN</td>
<td>21</td>
<td>0.8</td>
<td>4 × 10$^7$/2.5 (1 kHz)</td>
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<td>Polycrystalline Gd:HfO$_2$</td>
<td>3.4 cat%</td>
<td>ALD</td>
<td>27</td>
<td>300</td>
<td>N$_2$/800°C, 20 s</td>
<td>TaN/TaN</td>
<td>35</td>
<td>1.75</td>
<td>—</td>
<td>74</td>
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<tr>
<td>Polycrystalline Si:HfO$_2$</td>
<td>4.5 cat%</td>
<td>ALD</td>
<td>40</td>
<td>280</td>
<td>N$_2$/800°C, 10 min</td>
<td>TIN/TiN</td>
<td>5.1 (@80 K)</td>
<td>0.75</td>
<td>—</td>
<td>75</td>
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<tr>
<td>Polycrystalline Si:HfO$_2$</td>
<td>3.7 cat%</td>
<td>ALD</td>
<td>36</td>
<td>280</td>
<td>N$_2$/550–800°C, 20 s</td>
<td>TIN/TiN</td>
<td>12</td>
<td>1.0</td>
<td>10$^2$/4</td>
<td>76</td>
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<tr>
<td>Polycrystalline Mg:HfO$_2$</td>
<td>7.5 cat%</td>
<td>CSD (MOD)</td>
<td>42</td>
<td>215</td>
<td>Ar:O$_2$: 1:1/900°C</td>
<td>Pt/Pt</td>
<td>3</td>
<td>1</td>
<td>—</td>
<td>77</td>
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<tr>
<td>Polycrystalline Sr:HfO$_2$</td>
<td>7.5 cat%</td>
<td>CSD (MOD)</td>
<td>42</td>
<td>215</td>
<td>Ar:O$_2$: 1:1/900°C</td>
<td>Pt/Pt</td>
<td>12.8</td>
<td>1.5</td>
<td>—</td>
<td>77</td>
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<tr>
<td>Polycrystalline Ba:HfO$_2$</td>
<td>7.5 cat%</td>
<td>CSD (MOD)</td>
<td>42</td>
<td>215</td>
<td>Ar:O$_2$: 1:1/900°C</td>
<td>Pt/Pt</td>
<td>12</td>
<td>1.7</td>
<td>—</td>
<td>77</td>
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<tr>
<td>Polycrystalline Al:HfO$_2$</td>
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<td>CSD (MOD)</td>
<td>42</td>
<td>215</td>
<td>Ar:O$_2$: 1:1/900°C</td>
<td>Pt/Pt</td>
<td>3</td>
<td>0.7</td>
<td>—</td>
<td>77</td>
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<tr>
<td>Polycrystalline Ga:HfO$_2$</td>
<td>5.2 cat%</td>
<td>CSD (MOD)</td>
<td>42</td>
<td>215</td>
<td>Ar:O$_2$: 1:1/900°C</td>
<td>Pt/Pt</td>
<td>5</td>
<td>0.7</td>
<td>—</td>
<td>77</td>
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<tr>
<td>Polycrystalline In:HfO$_2$</td>
<td>5.2 cat%</td>
<td>CSD (MOD)</td>
<td>42</td>
<td>215</td>
<td>Ar:O$_2$: 1:1/900°C</td>
<td>Pt/Pt</td>
<td>5</td>
<td>0.7</td>
<td>—</td>
<td>77</td>
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<tr>
<td>Polycrystalline Si:HfO$_2$</td>
<td>6.0 mol%</td>
<td>ALD</td>
<td>10</td>
<td>280</td>
<td>N$_2$/800°C, 20 s</td>
<td>Pt/TiN/TiN</td>
<td>7 (@210 K)</td>
<td>3.5</td>
<td>10$^3$/4</td>
<td>78</td>
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<tr>
<td>Polycrystalline Si:HfO$_2$</td>
<td>1.6 mol%</td>
<td>PEALD</td>
<td>~10</td>
<td>200</td>
<td>N$_2$/800°C, 20 s</td>
<td>TaN/p-type Si(100) substrate</td>
<td>10 (under 5.5 MV)</td>
<td>10 (under 3.5 MV)</td>
<td>1</td>
<td>10$^3$/3.5</td>
</tr>
<tr>
<td>Polycrystalline Si:HfO$_2$</td>
<td>1.6 mol%</td>
<td>PEALD</td>
<td>~10</td>
<td>200</td>
<td>N$_2$/800°C, 20 s</td>
<td>TaN/p-type Ge(111) substrate</td>
<td>10 (under 3.5 MV)</td>
<td>1</td>
<td>10$^3$/3.5</td>
<td>79</td>
</tr>
<tr>
<td>Material</td>
<td>Doping cat%: dopant/(dopant + Hf)</td>
<td>Deposition method</td>
<td>Thickness (nm)</td>
<td>Deposition temperature °C</td>
<td>Annealing atmosphere/temperature</td>
<td>Deposition temperature °C</td>
<td>Top electrode/bottom electrode</td>
<td>El [MV cm⁻¹]</td>
<td>Pj [µC cm⁻²]</td>
<td>Endurance cycles/fatigue pulse height [MV cm⁻¹]</td>
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<td>Polycrystalline Y:HoO₂</td>
<td>0.9 mol%</td>
<td>Co-sputtering</td>
<td>12</td>
<td>(1.1 × 10⁻³ mbar)</td>
<td>N₂/1000 °C, 1 s</td>
<td>TiN/TiN</td>
<td>11</td>
<td>1.1</td>
<td>10</td>
<td>50</td>
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<tr>
<td>Polycrystalline Si:HoO₂</td>
<td>4 mol%</td>
<td>Metal organic ALD</td>
<td>10</td>
<td>1000 °C, 20 s</td>
<td>N₂/600 °C, 20 s (PMA)</td>
<td>TiN/TiN</td>
<td>&gt;10</td>
<td>1.2</td>
<td>10</td>
<td>1</td>
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<td>Polycrystalline Y:HoO₂</td>
<td>5.2 mol%</td>
<td>ALD</td>
<td>10</td>
<td>—</td>
<td>Vacuum (&gt;1 Pa), 700 °C, 1 min</td>
<td>TaN/TaN</td>
<td>9.9</td>
<td>0.79</td>
<td>10</td>
<td>80</td>
</tr>
<tr>
<td>Polycrystalline Y:HoO₂</td>
<td>3 mol%</td>
<td>Si implantation on RF sputtered HoO₂</td>
<td>10</td>
<td>—</td>
<td>N₂/600 °C, 20 s (PMA)</td>
<td>TaN/TaN</td>
<td>24</td>
<td>1.2</td>
<td>10</td>
<td>81</td>
</tr>
<tr>
<td>Polycrystalline Y:HoO₂</td>
<td>7 mol%</td>
<td>ALD</td>
<td>930</td>
<td>Room temp., P₃O₃ 10 mTorr</td>
<td>N₂/1000 °C, 10 s</td>
<td>Pt/[(111)Pt/TiOx/(001)Si]</td>
<td>14</td>
<td>1.45</td>
<td>—</td>
<td>82</td>
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<tr>
<td>Polycrystalline Sr:HoO₂</td>
<td>5 cat%</td>
<td>Sputtering</td>
<td>10</td>
<td>300</td>
<td>N₂/800 °C, 20 s</td>
<td>TiN/TiN</td>
<td>38.5</td>
<td>10⁻³/4.5</td>
<td>1.2</td>
<td>83</td>
</tr>
<tr>
<td>Epitaxial Y:HoO₂</td>
<td>7 mol%</td>
<td>RF sputtering</td>
<td>16</td>
<td>Room temp. ×</td>
<td>Pt/[(111)ITO/(111)YSZ]</td>
<td>TiN/TiN</td>
<td>15</td>
<td>2.5</td>
<td>10⁻³/4.5</td>
<td>84</td>
</tr>
<tr>
<td>Polycrystalline Y:HoO₂</td>
<td>0.53 at%</td>
<td>RF sputtering</td>
<td>5</td>
<td>—</td>
<td>N₂/600 °C, 30 s</td>
<td>TiN/p-type Ge</td>
<td>17.5</td>
<td>1.2</td>
<td>10⁻³/4.5</td>
<td>85</td>
</tr>
<tr>
<td>Polycrystalline Y:HoO₂</td>
<td>1.51 at%</td>
<td>RF sputtering</td>
<td>3</td>
<td>—</td>
<td>N₂/650 °C, 30 s</td>
<td>Au/p-type Ge</td>
<td>5</td>
<td>—</td>
<td>10⁻³/4.5</td>
<td>86</td>
</tr>
<tr>
<td>Polycrystalline Y:HoO₂</td>
<td>1.6 mol%</td>
<td>PEALD</td>
<td>10</td>
<td>200</td>
<td>N₂/800 °C, 20 s</td>
<td>TaN/TaN</td>
<td>9.5</td>
<td>1.2</td>
<td>10⁻³/4.5</td>
<td>86</td>
</tr>
<tr>
<td>Polycrystalline Si:HoO₂</td>
<td>1.6 mol%</td>
<td>ALD</td>
<td>10</td>
<td>200</td>
<td>N₂/800 °C, 20 s</td>
<td>TaN/TaN</td>
<td>9.5</td>
<td>1.2</td>
<td>10⁻³/4.5</td>
<td>86</td>
</tr>
<tr>
<td>Polycrystalline Gd:HoO₂</td>
<td>3.4 cat%</td>
<td>PEALD</td>
<td>27</td>
<td>300</td>
<td>N₂/650 °C, 20 s (PMA)</td>
<td>TiN/TiN</td>
<td>32.2</td>
<td>1.75</td>
<td>10⁻³/4.5</td>
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<tr>
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<td>7.1 cat%</td>
<td>ALD</td>
<td>8</td>
<td>300</td>
<td>N₂/850 °C, 1 min</td>
<td>SiO₂/SiO₂</td>
<td>22.5</td>
<td>1.75</td>
<td>10⁻³/4.5</td>
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<tr>
<td>Polycrystalline Si:HoO₂</td>
<td>5.65 mol%</td>
<td>PEALD</td>
<td>10</td>
<td>200</td>
<td>N₂/1000 °C</td>
<td>Ir/Ir</td>
<td>22</td>
<td>1.2</td>
<td>10⁻³/4.5</td>
<td>89</td>
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<tr>
<td>Polycrystalline Al:HoO₂</td>
<td>3 cat% Al</td>
<td>ALD</td>
<td>8.2</td>
<td>280</td>
<td>N₂/700 °C, 10 s</td>
<td>P₃/TiN</td>
<td>5.1</td>
<td>1</td>
<td>10⁻³/4.5</td>
<td>92</td>
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Table 2: Experimental reports on ferroelectric Hf$_{1-x}$Zr$_x$O$_2$ films in the literature

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<tr>
<td>Polycrystalline Hf$<em>{0.5}$Zr$</em>{0.5}$O$_2$</td>
<td>50 cat%</td>
<td>ALD</td>
<td>10</td>
<td>—</td>
<td>— / 800°C</td>
<td>TiN/TiN</td>
<td>25.51</td>
<td>1.085</td>
<td>—</td>
<td>55</td>
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<tr>
<td>Polycrystalline Hf$<em>{0.5}$Zr$</em>{0.5}$O$_2$</td>
<td>50 cat%</td>
<td>PEALD $O_2$/$H_2$ plasma deposition</td>
<td>10</td>
<td>200</td>
<td>N$_2$/500°C, 20 s</td>
<td>TiN/TiN</td>
<td>18</td>
<td>2</td>
<td>10$^7$/2</td>
<td>93</td>
</tr>
<tr>
<td>Polycrystalline Hf$<em>{0.42}$Zr$</em>{0.58}$O$_2$</td>
<td>58 cat%</td>
<td>PA-AOD atomic oxygen deposition</td>
<td>13</td>
<td>225</td>
<td>N$_2$/750°C, 20 s</td>
<td>TiN/Ge</td>
<td>34.63(30.6)</td>
<td>1.8</td>
<td>10$^7$/2.3</td>
<td>94</td>
</tr>
<tr>
<td>Polycrystalline Hf$<em>{0.5}$Zr$</em>{0.5}$O$_2$</td>
<td>50 cat%</td>
<td>PVD sputtering</td>
<td>11</td>
<td>Room temp.</td>
<td>N$_2$/450°C, 30 s</td>
<td>TiN/TiN</td>
<td>21.7</td>
<td>1.36</td>
<td>2 × 10$^6$/3.18</td>
<td>95</td>
</tr>
<tr>
<td>Polycrystalline Hf$<em>{0.5}$Zr$</em>{0.5}$O$_2$</td>
<td>50 cat%</td>
<td>ALD</td>
<td>10</td>
<td>200</td>
<td>N$_2$/600°C, 30 atm/30 min</td>
<td>TiN/TiN</td>
<td>21.5</td>
<td>1.61</td>
<td>—</td>
<td>96</td>
</tr>
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<td>Polycrystalline Hf$<em>{0.5}$Zr$</em>{0.5}$O$_2$</td>
<td>50 cat%</td>
<td>ALD</td>
<td>10</td>
<td>300</td>
<td>N$_2$/450°C, 30 atm</td>
<td>TiN/TiN</td>
<td>20.7</td>
<td>&lt;2</td>
<td>10$^7$/3.5</td>
<td>97</td>
</tr>
<tr>
<td>Polycrystalline Hf$<em>{0.5}$Zr$</em>{0.5}$O$_2$</td>
<td>50 cat%</td>
<td>ALD</td>
<td>10</td>
<td>300</td>
<td>N$_2$/450°C, 30 atm</td>
<td>TiN/TiN</td>
<td>20.7</td>
<td>&lt;2</td>
<td>10$^7$/3.5</td>
<td>97</td>
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**Notes:**
- ALD: Atomic Layer Deposition
- PEALD: Plasma-Enhanced Atomic Layer Deposition
- PVD: Physical Vapor Deposition
- PMA: Plasma-Induced Multilayer Formation
- Sputtering: Sputtering using 110 W power
- RF cosputtering: Reactive Ion Beam Sputtering
- Epitaxial-like ZrO$_2$/HfO$_2$/ZrO$_2$: Epitaxial-like ZrO$_2$/HfO$_2$/ZrO$_2$ layers
- Bilayers(STHZ): Bilayered STHZ layers
- Thickness ratio: Thickness ratio of HfO$_2$/ZrO$_2$
- Polycrystalline Hf$_{0.5}$Zr$_{0.5}$O$_2$: Polycrystalline Hf$_{0.5}$Zr$_{0.5}$O$_2$ layers
- ALD cycles: ALD cycles

**References:**
- Ref. [55]
- Ref. [93]
- Ref. [95]
- Ref. [97]
- Ref. [98]
- Ref. [99]
- Ref. [100]
- Ref. [101]
- Ref. [102]
- Ref. [103]
- Ref. [104]
- Ref. [105]
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<tr>
<td>Polycrystalline Hf$<em>{0.5}$Zr$</em>{0.5}$O$_2$/Al$<em>2$O$<em>3$/Hf$</em>{0.5}$Zr$</em>{0.5}$O$_2$</td>
<td>50 cat % Al$_2$O$_3$ inter-layer</td>
<td>ALD</td>
<td>40</td>
<td>280</td>
<td>N$_2$/400 °C</td>
<td>TiN/TiN</td>
<td>11.35</td>
<td>~1.37</td>
<td>10$^6$/2.5</td>
<td>116</td>
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<td>50 cat %</td>
<td>CVD</td>
<td>17</td>
<td>350</td>
<td>O$_2$/700 °C, 10 min</td>
<td>Pt/Pt</td>
<td>8</td>
<td>3</td>
<td>—</td>
<td>117</td>
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<td>Polycrystalline Hf$<em>{0.5}$Zr$</em>{0.5}$O$_2$</td>
<td>64 cat %</td>
<td>ALD</td>
<td>20</td>
<td>150</td>
<td>N$_2$/600 °C, 30 s</td>
<td>TaN/TaN</td>
<td>17.5</td>
<td>1.2</td>
<td>—</td>
<td>118</td>
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<tr>
<td>Polycrystalline Hf$<em>{0.5}$Zr$</em>{0.5}$O$_2$</td>
<td>50 cat %</td>
<td>PEALD</td>
<td>10</td>
<td>320</td>
<td>N$_2$/400 °C</td>
<td>TiN/TiN</td>
<td>14</td>
<td>1.4</td>
<td>—</td>
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<tr>
<td>Polycrystalline HfO$_2$</td>
<td></td>
<td>ALD</td>
<td>6</td>
<td>300</td>
<td>650 °C</td>
<td>TiN/TiN</td>
<td>10</td>
<td>1</td>
<td>10$^6$/2.5</td>
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<td>Polycrystalline ZrO$_2$</td>
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<td>RPALD</td>
<td>19.6</td>
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<td>N$_2$/600 °C, 30 s</td>
<td>Pt/Pt</td>
<td>12</td>
<td>1.5</td>
<td>—</td>
<td>54</td>
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<tr>
<td>Epitaxial (111)-ZrO$_2$</td>
<td></td>
<td>Sputtering</td>
<td>12</td>
<td>700, 200 W, 10 mTorr</td>
<td>×</td>
<td>Au/TiN/MgO(001)</td>
<td>5</td>
<td>0.5</td>
<td>—</td>
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<tr>
<td>Polycrystalline La$_x$(Hf,Zr)O$_2$</td>
<td>4.3 mol %</td>
<td>PEALD</td>
<td>10–13</td>
<td>280</td>
<td>N$_2$/600 °C, 1 min</td>
<td>Pt/Nb/LSMO</td>
<td>14</td>
<td>1.3</td>
<td>10$^6$/4</td>
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<td>Epitaxial Hf$<em>{0.5}$Zr$</em>{0.5}$O$_2$</td>
<td></td>
<td>PLD</td>
<td>6.9</td>
<td>800, $P_{O_2}$ 0.1 mbar</td>
<td>—</td>
<td>Pt/lN/TaN</td>
<td>24</td>
<td>3</td>
<td>—</td>
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<tr>
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<td>50 cat %</td>
<td>ALD</td>
<td>24</td>
<td>280</td>
<td>N$_2$/400 °C</td>
<td>TiN/TiN</td>
<td>6</td>
<td>2.8</td>
<td>—</td>
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<tr>
<td>Epitaxial Hf$<em>{0.5}$Zr$</em>{0.5}$O$_2$</td>
<td></td>
<td>PLD</td>
<td>7.7</td>
<td>675, $P_{O_2}$ 0.1 mbar</td>
<td>—</td>
<td>Pt/LSMO/STO/Si(001)</td>
<td>34</td>
<td>2.8</td>
<td>10$^6$/6.5</td>
<td>125</td>
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<tr>
<td>Epitaxial Hf$<em>{0.5}$Zr$</em>{0.5}$O$_2$</td>
<td></td>
<td>PLD</td>
<td>7.7</td>
<td>675, $P_{O_2}$ 0.1 mbar</td>
<td>—</td>
<td>Pt/LSMO/STO/Si(001)</td>
<td>15</td>
<td>2.8</td>
<td>10$^6$/5.2</td>
<td>125</td>
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<tr>
<td>Epitaxial rhombohedral(R3m) Hf$<em>{0.5}$Zr$</em>{0.5}$O$_2$</td>
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<td>PLD</td>
<td>5</td>
<td>—</td>
<td>—</td>
<td>Pt/LSMO/STO/Si(001)</td>
<td>34</td>
<td>5</td>
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<td></td>
<td>Sputtering</td>
<td>10</td>
<td>—</td>
<td>Vacuum (&lt;1 Pa)/600 °C</td>
<td>TaN/TaN</td>
<td>24</td>
<td>1</td>
<td>—</td>
<td>126</td>
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<tr>
<td>Polycrystalline HfO$_2$</td>
<td></td>
<td>ALD (with 10 s ozone dose)</td>
<td>6.9</td>
<td>260</td>
<td>N$_2$/650 °C, 1 min</td>
<td>TiN/TiN</td>
<td>13.5</td>
<td>1.5</td>
<td>—</td>
<td>127</td>
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<td>Polycrystalline Hf$<em>{0.5}$Zr$</em>{0.5}$O$_2$</td>
<td></td>
<td>MOCVD</td>
<td>16</td>
<td>350 4 Torr</td>
<td>Vacuum (&lt;1 Pa)/100 W</td>
<td>TiN/TiN</td>
<td>11.5</td>
<td>1.5</td>
<td>—</td>
<td>128</td>
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<tr>
<td>Polycrystalline HfO$_2$</td>
<td></td>
<td>Sputtering</td>
<td>20</td>
<td>1.2 $\times$ 10$^{-3}$ mbar</td>
<td>N$_2$/800 °C, 20 s</td>
<td>Ir/Ir</td>
<td>10.1</td>
<td>—</td>
<td>10$^6$/3</td>
<td>53</td>
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first experimental report on ferroelectricity in Si-doped HfO₂. In 1999, Lowther et al.-reported that the polar Pca2₁ orthorhombic phase could have lower free energy than the stable monoclinic phase under a high hydrostatic pressure condition of ~4 GPa. However, no experimental confirmation had been made at that time.

Huan et al. recently reexamined the free energy of various crystalline phases of HfO₂ in a wide temperature and pressure range. They reported that the free energy differences between the two polar orthorhombic phases (space groups: Pca2₁ and Pmn2₁) and the stable monoclinic phase are smaller than k₄T₁S, where k₄ and T are the Boltzmann constant and temperature, respectively. They also suggested that the relatively low free energy barrier between the two phases could be readily overcome by doping and strain. From the simulated X-ray diffraction (XRD) patterns of Pca2₁, and Pmn2₁ orthorhombic phases, the frequently observed XRD patterns of polycrystalline films were better matched with that of the Pca2₁ orthorhombic phase, which Boescke et al. first suggested as the origin of the unexpected ferroelectric phase formation. The XRD pattern of the Pmn2₁ orthorhombic phase is quite similar to that of the stable monoclinic phase, especially for the 2θ of 25–35° region. Thus, the usually observed ferroelectricity in doped-HfO₂ thin films should be attributed to the formation of the polar Pca2₁ phase.

Another interesting possible polar phase is the rhombohedral phase (space group: R3m) which was first observed by Wei et al. in epitaxial HfₓZr₁₋ₓO₂ thin films formed on a LSMO/STO substrate. Although this phase could show interesting properties with a high Pₑ of 34 μC cm⁻², the phase was so far only reported for epitaxial films. The focus of this review, therefore, will be on the Pca2₁ orthorhombic phase, which has been most frequently reported in polycrystalline films.

It should be noted that the free energy of the Pca2₁ phase was always higher than that of the monoclinic phase in Huan et al.’s work, although the difference was not large. Therefore, various other factors including doping, surface energy, hydrostatic pressure, biaxial film stress, and electric field have been examined by several research groups to explain the stabilization of the orthorhombic phase. Reyes-Lillo et al. examined the free energy of various crystalline phases in HfO₂ and ZrO₂, and showed that the free energy difference between the metastable and stable phases is much smaller in ZrO₂ than in HfO₂. This was suggested as a possible explanation for the origin of antiferroelectric hysteresis observed in ZrO₂. The antiferroelectric-like behavior in ZrO₂ could be attributed to the field-induced phase transition between the tetragonal and orthorhombic phases. This report implied that the free energy difference between the Pca₂₁ orthorhombic phase and the monoclinic phase should decrease with increasing Zr concentration in Hf₁₋ₓZrₓO₂ solid solutions.

Materlik et al. systematically examined the free energy of various crystalline phases of HfO₂, HfₓZr₁₋ₓO₂, and ZrO₂ by considering various factors including temperature, hydrostatic pressure, biaxial film stress, and free surface energy. They showed that the free energy of the ferroelectric orthorhombic phase could be decreased with increasing Zr content in the Hf₁₋ₓZrₓO₂ system, and it can be even lower than that of the monoclinic phase when the contribution of free surface energy is considered. The effects of hydrostatic pressure and biaxial film stress were much weaker compared to that of the free surface energy.

Batra et al. also reported their theoretical calculation to show that the Pca2₁ orthorhombic phase can be thermodynamically stabilized by biaxial compressive strain and electric field. The appropriate application of the two factors could decrease the bulk free energy of the polar orthorhombic phase even below that of the monoclinic phase. In another work, Batra et al. systematically examined the dopants’ effect on the free energy of the different crystalline phases of HfO₂ via high throughput calculations. They examined various cations in the periodic table as potential dopants in HfO₂ with 3.125 cat% (dopant/(dopant + Hf)) concentration, and selected 6 promising dopants (Ca, Sr, Ba, Y, La and Gd). The 6 dopants could decrease the free energy of polar orthorhombic phases (Pca₂₁, and Pmn2₁) most effectively with the help of the accompanying oxygen vacancy effect.

Fig. 1 shows the free energy of the different crystalline phases as a function of doping concentration of (a) Ca, (b) Sr, (c) Ba, (d) Y, (e) La and (f) Gd from Batra et al.’s work. In pure HfO₂, the free energy of the Pca₂₁ orthorhombic phase is higher than that of the stable monoclinic phase by ~ 83.3 meV per f.u. and 81.9 meV per f.u. at 0 K and 300 K. The polar orthorhombic phase could be thermodynamically stabilized, as shown by the free energy of the ferroelectric phases. Note that P-O₁ and P-O₂ phases in Fig. 1 are Pca₂₁ and Pmn2₁ orthorhombic phases, respectively, where the total energy of the orthorhombic phase was lower than that of the monoclinic phase under the specific conditions. Unfortunately, some of the simulated XRD patterns were very much distorted to indicate the exact crystalline...
structure distinctively, which are shown as open symbols in Fig. 1. The inclusion of a dopant atom induced distortion of chemical bonds in the material’s unit cell. For the cases of Ca and La doping, the ‘distorted’ Pca21 orthorhombic phase showed the lowest free energy.

To summarize, from the computational simulations, it could be understood that the free energy difference between the meta-stable polar orthorhombic phases and the stable monoclinic phase decreases with increasing doping concentration. Nonetheless, the difference in free energy among the known phases was still too high to explain the stabilization of the ferroelectric orthorhombic phase by thermodynamic arguments alone.

Kinetic effect

The unexpected metastable phase formation does not necessarily originate from thermodynamic stabilization. Park et al. suggested a kinetic model describing the unusual ferroelectric orthorhombic phase formation based on the well-known Ostwald’s step rule. In the suggested model, the ferroelectric orthorhombic phase does not necessarily need to have the lowest free energy among the various crystalline phases. In the kinetic model, they firstly indicated that the relative fraction of the monoclinic phase which is altered by the annealing temperature does not follow the thermodynamic consideration. While thermodynamics predicted a decrease in the monoclinic phase fraction with increasing temperature, experimental observations showed an opposite trend.

To explain such peculiar behavior, they proposed a phase transition in two steps during film crystallization through a rapid thermal process (RTP): (1) crystallization process with transition from the amorphous to tetragonal phase during the RTP, and (2) tetragonal to orthorhombic or monoclinic phase transition during cooling when the tetragonal phase was firstly formed as shown in Fig. 2a. Through quantitative consideration based on a classical nucleation model, two conditions for the ferroelectric orthorhombic phase formation could be identified.

First, the doping concentration should be sufficiently high to induce amorphous to tetragonal phase transition. It was shown that if the amorphous phase transforms directly to the monoclinic phase during the RTP, the subsequent transformation into any other crystalline phase is unlikely. It should be noted that the direct phase transition from an amorphous to a monoclinic phase is normally improbable, but the in situ X-ray diffraction experiment revealed a direct amorphous-to-monoclinic phase transition. However, the formation of metastable intermediate phases for a short period of time below the detection limit of XRD cannot be excluded completely. Second, the doping concentration should be sufficiently low to allow the tetragonal to orthorhombic phase transition. Through this process, the dominant transformation from amorphous to orthorhombic phase through the intermediate tetragonal phase can be understood.

Fig. 2b–e shows the comparison of the expected remanent polarization (P r) from Park et al.’s model, which was based on the classical nucleation and nucleation-limited phase transition theory, and experimental P r for Y, Sr, La, and Ge doped HfO 2. Although there exist quantitative differences between the theoretical expectation and experimental observations, the qualitative trends showed a reasonable good agreement. The quantitative difference may originate from the inaccuracy of the assumed physical parameters for the modeling. Moreover, it was reported that the locally distorted structure could be different from the average crystalline structure analyzed using macroscopic X-ray diffraction.

The kinetic model suggests a key to understanding the discrepancy between experimental observations and theoretical works based on thermodynamic free energy. According to the kinetic model, the Pca21 orthorhombic phase does not need to have the lowest bulk energy to be stabilized. Lee et al. experimentally examined the kinetics of phase transition in Hf0.5Zr0.5O2 thin films, and demonstrated that the transition from the tetragonal/orthorhombic to the monoclinic phase is nucleation limited. The thermodynamic and kinetic mechanisms will be further discussed in the following sections, which deal with the effects of various defects on the formation mechanism of the polymorphism in fluorite-structure ferroelectrics.

Point defects

Oxygen vacancies

Oxygen vacancies (V O) are a native defect of metal oxides, especially transition metal oxides, and are perhaps the most interesting defect in fluoride-structure oxides. Before the discovery of the ferroelectric phase in doped-HfO 2, the critical role of V O in high-k gate dielectrics with HfO 2 had been extensively studied. The presence of V O’s in the metal/high-k HfO 2/Si causes bulk traps which induce hysteresis in the drain current–gate voltage transfer curve of MOSFETs. As a result, decreasing the V O concentration was essential to optimize the electrical properties of MOSFETs.

In ferroelectric HfO 2, V O’s are reported to affect polymorphism as well as electrical properties, and thus, they are considered
even more important than those in MOSFETs’ gate oxides. Due to the rather high coercive field (\( \sim 0.8–2 \text{ MV cm}^{-1} \)) of ferroelectric doped \( \text{HfO}_2 \), a high switching electric field should be applied in the normal operation of the ferroelectric devices. Under such a circumstance, oxygen vacancies drift and percolate during repetitive polarization switching or even under DC bias. The movement of Vo upon application of an electric field was suggested as the origin of some of the key reliability issues of ferroelectric doped \( \text{HfO}_2 \), such as the so-called “wake-up effect” and limited endurance with hard breakdown.\(^{6,136–138}\) More information on these topics can be found in other recent reviews and book chapters.\(^{3,4,139}\) In this section, therefore, the focus will be on the important roles of oxygen vacancies in the polymorphism of fluorite-structure oxides based on existing theoretical and experimental works.

Hoffmann et al.\(^{74}\) reported that the remanent polarization of Gd-doped HfO\(_2\) could be improved by replacing the TiN top and bottom electrodes with TaN electrodes. They also reported the effect of Vo concentration on the free energy of various crystalline phases, including monoclinic, orthorhombic, and tetragonal phases. From computational simulations, the free energy of the tetragonal and orthorhombic phases decreased with increasing oxygen vacancy concentration. They suggested that TaN can reduce Gd-doped HfO\(_2\) more strongly than TiN, and the resulting higher Vo concentration is the origin of the improved P\(_r\) in structures with TaN top and bottom electrodes. Although it was a reasonable conclusion, the quantity of Vo in Gd-doped HfO\(_2\) was not addressed. According to computational simulations, a significant effect of Vo is expected for its concentration higher than 6.25%. This value is unreasonably high compared to the experimentally observed ones. It should be noted that 3.125% is the minimum vacancy concentration, which can be taken into consideration in the density functional calculations with 96 atoms (\( 2 \times 2 \times 2 \) unit cells). When assuming a linear relationship between the absence of vacancies and 3.125% vacancies case, general trends can be understood.

Lee et al.\(^{140}\) deposited ferroelectric Hf\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) thin films by physical vapor deposition (PVD) in various O\(_2\)/(Ar + O\(_2\)) flow rate ratio atmospheres, which is expected to affect the oxygen vacancy concentration in the as-deposited films. Fig. 3 shows the polarization vs. electric field curves of Hf\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) thin films sputtered under an O\(_2\)/(Ar + O\(_2\)) flow rate of (a) 0, (b) 1.67, (c) 2.5, and (d) 3.33%, respectively. Changes in (e) film density (analysed using X-ray reflectivity) and deposition rate, (f) average grain size, and (g) dielectric constant, \( \varepsilon_r \) and m-phase fraction as a function of O\(_2\)/(Ar + O\(_2\)) flow rate, respectively. Data are from ref. 140.

Fig. 3  Polarization–electric field curves of TiN/Hf\(_{0.5}\)Zr\(_{0.8}\)O\(_2\)/TiN capacitors with Hf\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) films sputtered with an O\(_2\)/(Ar + O\(_2\)) flow rate of (a) 0, (b) 1.67, (c) 2.5, and (d) 3.33%, respectively. Changes in (e) film density (analysed using X-ray reflectivity) and deposition rate, (f) average grain size, and (g) dielectric constant, \( 2\varepsilon_r \) and m-phase fraction as a function of O\(_2\)/(Ar + O\(_2\)) flow rate, respectively. Data are from ref. 140.

Pal et al.\(^{127}\) examined the effect of ozone dose time on the ferroelectric properties of ALD undoped HfO\(_2\) films, which should affect the Vo concentration in HfO\(_2\). When the ozone dose time increased from 5 to 40 s, the \( P_r \) value decreased from \( \sim 14 \) to \( \sim 6 \text{ \mu C cm}^{-2} \). They quantitatively examined the Vo concentration from DC current-voltage measurements, assuming the trap-assisted-tunneling conduction. The estimated oxygen vacancy concentration decreased from \( 2 \times 10^{18} \) to \( 2 \times 10^{16} \text{ cm}^{-3} \) when ozone dose time increased from 5 to 40 s. The highest Vo concentration corresponding to 5 s ozone dose time was calculated to be only 0.03% of the oxygen positions. This quantity is lower than the concentration considered in Hoffmann et al.’s work by \( \sim 2 \) orders of magnitude.\(^{74}\)

Schoedel et al.\(^{141}\) and Materano et al.\(^{142}\) also evaluated the impact of O\(_2\) pulse time on the phase and reliability behavior of Hf\(_{1-x}\)Zr\(_x\)O\(_2\) films. Longer O\(_3\) pulse time caused a transition from tetragonal phase portions to orthorhombic and monoclinic phase portions. At the same time, the number of polarization switching cycles before reaching hard breakdown and a specific leakage current density values were improved, which could be
attributed to a reduced $V_{O}$ concentration for longer $O_3$ pulse times.

Fengler et al.\textsuperscript{143} examined the concentration of mobile $V_{O}$ using thermally stimulated depolarization current measurements (TSDC). TSDC measurements enabled the extraction of the concentration of singly and doubly charged $V_{O}$ which can drift under DC bias. The results showed the concentrations of singly and doubly charged oxygen vacancies of 0.26 and 0.1\%, respectively.\textsuperscript{143} Such values are ~1 order of magnitude higher than those measured by Pal et al.\textsuperscript{127} Fengler et al. also suggested that both imprint and wake-up could be attributed to the charged defects ($V_{O}$) near the top electrode and their redistribution during repetitive electric field cycling.\textsuperscript{144} They suggested that most of the oxygen vacancies are neutral or immobile under the investigated electric field (up to 1.5 MV cm$^{-1}$) and temperature ranges (up to 380 °C).\textsuperscript{141} Comparing the total concentration of the charged vacancies as determined by TSDC (~0.4\%)\textsuperscript{141} and that of the neutral vacancies at the HfO$_2$ based dielectric/TiN interface (~0.7\%)\textsuperscript{144} a higher concentration of neutral vacancies can be assumed. Charged vacancies are expected to serve as pinning sites for the domain wall motions. The concentration of charged and uncharged vacancies increased after electric field cycling, suggesting that $V_{O}$'s are the cause for the instability of ferroelectricity of HfO$_2$-based thin films manifesting as fatigue and breakdown.\textsuperscript{143}

Homouda et al.\textsuperscript{144} systematically analyzed the $V_{O}$ concentration at the TiN/Hf$_{0.7}$Zr$_{0.3}$O$_2$ interfacial regions using emission angle-dependent X-ray photoelectron spectroscopy (XPS) on Hf$_{0.7}$Zr$_{0.3}$O$_2$ films coated with a 2 nm-thick TiN layer. Since the probing depth is strongly affected by the emission angle, the relative intensity ratio of binding energy peaks from TiN and TiO$_x$N$_y$ could be compared at various emission angles. From the result, the partial oxidation of TiN could be confirmed, and the maximum oxygen vacancy concentration at the topmost 1 nm of Hf$_{0.7}$Zr$_{0.3}$O$_2$ was ~0.7\%, which was 2–3 times higher than the one reported by Fengler et al.\textsuperscript{143} They suggested that the bottom TiN electrode was already partially oxidized during the ALD process due to the oxygen source injection, whereas the top electrode was not exposed to the oxygen source since it was deposited after the ALD process. During the RTP for film crystallization, the top interfacial Hf$_{0.7}$Zr$_{0.3}$O$_2$ can be reduced by the oxygen scavenging effect of the top TiN electrode. Because the bottom TiN electrode was already oxidized, the scavenging effect was predicted to be much weaker at the bottom interface.\textsuperscript{144} The effect of annealing temperature on the redistribution of $V_{O}$ has also been investigated.\textsuperscript{76,86,145}

From the experimental reports above, the oxygen deficient atmosphere during film deposition, i.e., low oxidant dose times for ALD or low oxygen flow rate for sputtering, is harmful in achieving stronger ferroelectricity with a higher fraction of the ferroelectric orthorhombic phase. Qualitatively, this trend can be well understood and seems to be consistent with the theoretical calculations introduced above. However, it should also be noted that there exists a quantitative difference between theoretically expected oxygen vacancy concentration required for ferroelectric phase stabilization and experimentally measured oxygen vacancy concentration.

One possible explanation to mitigate the gap between theoretical and experimental works is the inhomogeneous distribution of oxygen vacancies. It was reported that the oxygen vacancy concentration in the as-fabricated metal–ferroelectric-metal capacitors is the highest at the metal-ferroelectric interfaces. Moreover, the interfacial region should be prone to serve as the nucleation site, given its high defect concentration. As a result, the nucleation at the interfacial region seems to be more strongly affected by the averaged $V_{O}$ concentration.

Recently, Zhou et al.\textsuperscript{146} reported interesting computational simulation results on $V_{O}$'s with respect to their location in metal/ferroelectric/metal stacks. They reported that the formation energy of $V_{O}$ at the HfO$_2$/TiN interface (~0.8 eV) is much lower than that in the film bulk region (~2.8 eV), suggesting that the $V_{O}$ concentration is expected to be much higher at the HfO$_2$/TiN interface than that in the bulk part of films. This difference could amount to ~9 orders of magnitude.\textsuperscript{144} Such a trend was previously suggested by Cho et al.\textsuperscript{147} before the discovery of ferroelectricity in doped HfO$_2$ systems. These theoretical works support the above-mentioned hypothesis on the nucleation at the interfacial region with a high $V_{O}$ concentration.

To summarize, the $V_{O}$ concentration strongly affects the ferroelectric phase formation in fluorite-structure oxides by affecting the free carrier energy values of various crystalline phases, and by decreasing the grain size or serving as preferred defective nucleation sites. A high oxygen vacancy concentration is expected especially at the ferroelectric/metal interfaces, and the dominant nucleation at the interfacial region could be the reason why the effect of oxygen $V_{O}$ seems to be much stronger than theoretical predictions.

On the other hand, a high $V_{O}$ concentration in the ferroelectric orthorhombic phase, once it has been stabilized, is expected to degrade the ferroelectric behavior. Ferroelectric polarization is based on sub-unit-cell motion of ions according to the applied bias polarity, so it should be decreased by increasing $V_{O}$ concentration. It was also reported that the dielectric relaxation of ferroelectric materials is associated with the long-range motion and the short-range hopping of the oxygen vacancies.\textsuperscript{148} Moreover, the $V_{O}$ is one of the origins of trap levels in the electrical bandgap, which significantly affect the carrier conduction via several mechanisms, including trap assisted tunneling and Poole–Frenkel emission. Therefore, increasing the ferroelectric orthorhombic phase fraction without increasing the oxygen vacancy concentration would be a more appropriate strategy for achieving electronic devices based on fluorite-structure ferroelectrics.

**Carbon**

Besides the native defects ($V_{O}$), extrinsic defects originating from the material synthesis process are also highly important in understanding the fluorite-structure ferroelectrics. Carbon is a common residual impurity in ALD films. In many research papers on ALD of the ferroelectric doped HfO$_2$ films, metal-organic precursors such as Hf[N(CH$_3$)$_2$]$_4$ (TEMA-Hf), Hf[N(CH$_3$)$_3$]$_4$ (TDMA-Hf), and C$_4$Hf[N(CH$_3$)$_3$]$_3$ have been...
utilized. ALD is based on a characteristic self-saturated mechanism with chemical reactions between metal precursors, oxygen sources such as H2O, O3, and O2 plasma, and substrates or previously deposited films. Ideally, the organic ligands of metal–organic precursors are completely removed during the oxygen source injection step and the following purge process. However, residual impurities, including C, N, and H, could be included in the layer due to imperfect chemical reactions.

Kuenneth et al. examined the effect of carbon concentration in HfO2 on the free energy values of the various crystalline phases. They supposed that C replaces Hf with a concentration of 3.125 and 6.25%, but the free energy difference between ferroelectric orthorhombic and monoclinic phases slightly increased, suggesting that doping C as a substitutitional dopant is not useful to induce ferroelectricity in HfO2. However, other forms of C doping, including interstitial C, were not considered in that report. Again, it should be noted that 3.125% is the minimum vacancy concentration which can be considered in a density functional theory work with 96 atoms (2 × 2 × 2 unit cells).

The C-effect has been studied in the field of high-k gate oxides to see if the C impurity can enhance the formation of the tetragonal phase over the monoclinic phase because the former has a k value almost double of the latter. Jung et al. examined the effect of C incorporation into Hf-substitutitional, O-substitutitional, and interstitial sites on the free energy difference between the tetragonal and monoclinic phase. From their result, C incorporation into the interstitial sites or oxygen-substitutitional positions could decrease the free energy of the tetragonal phase further compared to Hf substitution. In that work, the combined effect from C impurity and doubly charged V0 could most significantly decrease the free energy of the tetragonal phase. Thus, a more substantial impact when C is incorporated in a different configuration cannot be excluded solely from Kuenneth et al.’s work. This topic requires further study.

Unlike the theoretical studies, several experimental studies have shown that the ferroelectricity in doped HfO2 is strongly affected by C impurities. Kim et al. examined the effect of deposition temperature of the ALD process on the phase evolution and the accompanying ferroelectric performance of HfO2 and Hf0.5Zr0.5O2 films. Fig. 4 shows the evolution of polarization vs. electric field curves of HfO2 (Fig. 4a–c) and Hf0.5Zr0.5O2 (Fig. 4f–i) films with varying deposition temperature from 280 to 200 °C. Fig. 4j–l show the changes in C concentration, average grain size and 2P, values as a function of deposition temperature, respectively. As shown in Fig. 4a–c, Hf0.5Zr0.5O2 showed strong ferroelectricity with a P of > 10 μC cm⁻² with a high orthorhombic phase fraction at the deposition temperature of 280 °C, but antiferroelectric-like double hysteresis originating from the field-induced phase transition between the tetragonal and orthorhombic phase or depolarization fields at the deposition temperature of 200 °C. This result suggests that at zero electric field the dominant crystalline phase of Hf0.5Zr0.5O2 films deposited at 280 and 200 °C is the orthorhombic and tetragonal phase, respectively.

HfO2 thin films showed linear dielectric behavior with a high monoclinic phase fraction at the deposition temperature of 280 °C, whereas robust ferroelectricity with a P of > 10 μC cm⁻² could be observed at the deposition temperature of 220 °C with a lower monoclinic phase fraction compared to films deposited at 280 °C. The observed change in the P value seems the opposite for Hf0.5Zr0.5O2 and HfO2, but fits the general trend as reported by Materano et al. and Schroeder et al. for V0. Adding more carbon to Hf0.5Zr1−xO2 resulted in a similar phase transition from the monoclinic to orthorhombic to the tetragonal phase. The large P of HfO2 deposited at 220 °C suggests that the high orthorhombic phase fraction with the resulting large P can be induced even without cationic doping which has been generally required for ferroelectricity in HfO2.

To understand the substantial effect of deposition temperature, the chemical composition of HfO2 and Hf0.5Zr0.5O2 films was examined using Auger electron spectrometry (AES) as shown in Fig. 4. The C concentration increased with decreasing deposition temperature from 260 to 180 °C, suggesting that the removal of the organic ligands during ALD was kinetically retarded with decreasing deposition temperature. The slightly higher C concentration in the 280 °C deposited Hf0.5Zr0.5O2 thin film compared to the one deposited at 260 °C could be attributed to the chemical vapor deposition-like thermal decomposition of metal–organic precursors.

To examine the effect of residual C concentration on the average grain size of the Hf0.5Zr0.5O2 film, planar scanning electron microscopy images were analyzed using a watershed method implemented by Gwyddion software, and 2P values as a function of deposition temperature. Data are from ref. 26 and 52.
significant, but a slight decrease could be confirmed. It should be noted that even a small difference in grain radius can significantly affect the polymorphism when the free energy difference between the competing crystalline phases is small. Moreover, the residual defects such as C, N, and H might have thermodynamic effects on the free energy of various crystalline phases. Thus, the combined effect of the chemical purity and the accompanying microstructural change could be sufficient for the significant change in polymorphism and the resulting ferroelectricity, shown in Fig. 4.

Cho et al.\textsuperscript{152} reported the influence of C concentration in HfO\textsubscript{2} films on the film microstructure and the accompanying phase change which were grown by an ALD process with TEMA and ozone. Decreasing the ozone generator power retarded the decomposition of ligands in the metal–organic precursor, which resulted in a higher relative fraction of the metastable tetragonal phase over the stable monoclinic phase. This could be attributed to the decrease in the average grain size since the residual C impurities interfered with the growth of grains.\textsuperscript{152} They suggested that the metastable tetragonal phase can be stabilized due to the grain boundary energy effect, although they did not directly examine the grain size of the HfO\textsubscript{2} films.

The species and concentrations of residual impurities in ALD films are also closely related to the type of metal precursors used and their chemical reactivity. Several Hf precursors such as TEMA-Hf, TDMA-Hf, \( \text{C}_2\text{Zr}[\text{N}({\text{CH}}_3)]_3 \), and HfCl\textsubscript{4} have been utilized for the deposition of ferroelectric doped HfO\textsubscript{2} thin films.

Materano et al.\textsuperscript{153} comparatively studied the chemical, physical, and ferroelectric properties of Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} thin films deposited using various precursors including TEMA-M, TDMA-M, C\textsubscript{2}M[\text{N}({\text{CH}}_3)]\textsubscript{3}, and MCl\textsubscript{4}, where M is Hf or Zr. The ferroelectric properties could be reproduced with all precursors studied, but there exist differences in the impurity concentration, the optimal range of deposition temperature, the composition for maximum polarization, film density of as-deposited films and the achievable maximum ferroelectric orthorhombic phase fraction. The optimized temperature range was dependent on the chemical nature of the metal–organic precursors. From the result, for low deposition temperature application, TEMA-M-based precursors show stable ALD growth, whereas for higher deposition temperatures, C\textsubscript{2}M[\text{N}({\text{CH}}_3)]\textsubscript{3} or MCl\textsubscript{4}-based processes are favourable.

Kim and Hyun et al.\textsuperscript{154} compared the chemical and electrical properties of Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} thin films deposited using TEMA-M and TDMA-M precursors. Fig. 5a and b show the \( P-E \) curves achieved during the endurance test with the increasing number of 3.0 MV cm\textsuperscript{-1}-high bipolar fatigue pulses at a frequency of 100 kHz for TiN/Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2}/TiN capacitors with Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} deposited using (a) TDMA-M and (b) TEMA-M precursors. The \( P-E \) measurement frequency and electric field were 1 kHz and \( \sim 3.8 \text{ MV cm}^{-1} \), respectively. When the \( P-E \) curves measured in a pristine state (before wake-up field cycling) are compared, the TDMA-M sample showed more square-like \( P-E \) hysteresis with a \( P_r \) of \( \sim 21 \text{ μC cm}^{-2} \), whereas the TEMA-M sample showed a distorted \( P-E \) curve (black curve in Fig. 5b) with a \( P_r \) of \( \sim 16 \text{ μC cm}^{-2} \).

After 10\textsuperscript{4} wake-up field cycles, the \( P_r \) value increased up to 26 and 22 μC cm\textsuperscript{-2} for TDMA-M and TEMA-M samples, and the evolution in \( P_r \) values normalized by the \( P_r \) value after the wake-up process is shown in Fig. 5c. The pristine \( P_r \) values were 81 and 69% of the \( P_r \) values after wake-up field cycling for TDMA-M and TEMA-M samples, respectively. This result suggested that the Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} film deposited using TDMA-M precursors was better optimized with less impurity concentration and/or lower relative fraction of the non-ferroelectric phase in the pristine state compared to the Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} film deposited using TEMA-M precursors. From chemical analysis, it was proven that the C concentration in TDMA-M Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} (\( \sim 2.2% \)) was lower than that in TEMA-M Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} (\( \sim 4.0% \)). These results seemed contradictory to the results achieved by Kim et al.\textsuperscript{26} and Cho et al.,\textsuperscript{152} where the presence of C in the ALD process, induced by either the lower growth temperature or lower ozone concentration, was essential to achieve the ferroelectric orthorhombic phase and suppress the monoclinic phase. However, it should be noted that in the work by Kim and Hyun et al.,\textsuperscript{154} the growth temperature and ozone concentration were identical, but only the residual carbon concentration was varied. In fact, the competing phases were not the orthorhombic and monoclinic phases, but the orthorhombic and tetragonal phases. In this case, the smaller grain size, which was achieved when a slightly higher C concentration was used, preferred the tetragonal phase over the orthorhombic phase, which would be preferred for the slightly larger grain size with lower C impurity concentration.

C impurities in HfO\textsubscript{2} are also known to affect the leakage current density. With lower C concentration, TDMA-M Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} showed lower leakage current density than TEMA-M Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2}, especially in the low electric field region, as shown in Fig. 5d. Moreover, from the endurance test results in Fig. 5e and f, TDMA-M Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} could endure more than 10\textsuperscript{9} field cycles.

![Fig. 5 Polarization–electric field (\( P-E \)) curves of (a) TDMA HZO and (b) TEMA HZO capacitors measured in the pristine state and fatigued states pulsed 10\textsuperscript{2}, 10\textsuperscript{3}, 10\textsuperscript{4}, and 10\textsuperscript{5} times by 3.8 MV cm\textsuperscript{-1}-high and 10 μs-wide bipolar rectangular pulses. (c) Changes in \( P_r \), values of TDMA (black) and TEMA (red) HZO capacitors as a function of fatigue pulses. (d) Current density–electric field curves of TDMA HZO (black) and TEMA HZO (red). The results of the endurance test of (e) TEMA HZO and (f) TDMA HZO with electric field cycling using a pulse field amplitude of 2.5 and 3.0 MV cm\textsuperscript{-1}. The frequency of the rectangular double pulse for the endurance test was fixed at 100 kHz. Data are from ref. 154.](image-url)
using bipolar pulses of 100 kHz frequency and 2.5 MV cm\(^{-1}\) height.

To summarize, C is an important defect in ferroelectric doped HfO\(_2\) since it can affect the ferroelectricity by being incorporated in the interstitial sites, O-substitutional sites, and Hf-substitutional sites. To the authors’ knowledge, no computational simulation has yet elucidated the effect of C concentration at the various aforementioned sites on the ferroelectric phase formation. Therefore, it requires further study. However, several experimental studies demonstrated that C incorporation suppressed the stable monoclinic phase formation and induced ferroelectric phase in HfO\(_2\) with low doping concentration. For ferroelectric doped HfO\(_2\), on the other hand, a very high residual C could increase the relative fraction of the tetragonal phase at the expense of the orthorhombic phase so that \(P_r\) decreases. C incorporation can also degrade the electrical reliability of the devices. Overall, the effect of C impurity on polymorphism is similar to doping and oxygen vacancies. On the other hand, residual C can act as pinning sites for domain wall motion, which will potentially decrease the operation speed and reliability of electronic devices based on fluorite-structure oxides. Such deleterious effects are compounded by the fact that C can contribute to the electronic conduction based on Poole–Frenkel emission or trap-assisted-tunneling by forming trap levels in the electrical bandgap.

Hydrogen

Hydrogen is another important residual impurity that can originate from organic ligands of the metal–organic precursors, oxygen source, and/or annealing atmosphere. For the case of conventional perovskite-structure ferroelectrics, the ferroelectric properties are severely degraded by hydrogen impurities.\(^{153–157}\) The incorporation of hydrogen at the interstitial sites can completely remove ferroelectricity in perovskite-structured ferroelectric oxides. The interstitial hydrogen atoms or protons severely disturb the sub-unit-cell motion of ions in perovskites causing the loss of polarization reversal. Even worse, the ferroelectric oxides can be reduced with the formation of a conducting metal-rich phase by hydrogen annealing.

When ferroelectric HfO\(_2\) is implemented in practical semiconductor devices with a Si channel such as FeFETs, annealing in a hydrogen atmosphere is essential to remove interfacial states originating from the imperfections at the gate oxide/Si interface. Thus, understanding the effects of hydrogen impurities in ferroelectric doped HfO\(_2\) thin films is crucial for their practical application.

Park et al.\(^{158}\) examined the effect of forming gas (95% N\(_2\) + 5% H\(_2\)) annealing on the ferroelectric properties of Hf\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) films with Pt and TiN top electrodes. Fig. 6a–d show the \(P–V\) curves of Pt/Hf\(_{0.5}\)Zr\(_{0.5}\)O\(_2\)/TiN capacitors annealed in forming gas (95% N\(_2\) + 5% H\(_2\)) at the temperature of 300–600 °C, and Fig. 6e–h show the \(P–V\) curves of Pt/TiN/Hf\(_{0.5}\)Zr\(_{0.5}\)O\(_2\)/TiN capacitors annealed under the same atmosphere, respectively. It could be understood that the forming gas annealing (FGA) indeed degraded the ferroelectric performance, but it was much less severe compared with the perovskite oxide cases.

Fig. 6a–d confirmed that the \(P_r\) value decreases with the decreasing temperature of FGA from 600 to 300 °C, which is also in stark contrast to the case of perovskite ferroelectrics. This result suggests that when the Pt top electrode directly contacts the ferroelectric Hf\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) film, \(P_r\) is degraded by up to 9 μC cm\(^{-2}\) (~45% of the original 2\(P_r\)) at the FGA temperature of 300 °C. For the cases of Pt/TiN/Hf\(_{0.5}\)Zr\(_{0.5}\)O\(_2\)/TiN capacitors, on the other hand, the maximum degradation of 2\(P_r\) is ~17% (~6 μC cm\(^{-2}\)) of the original 2\(P_r\) before FGA as summarized in Fig. 6i. In contrast, during N\(_2\) annealing, the 2\(P_r\) value seemed independent of the annealing temperature.

Fig. 6j and k show the XPS spectra of Zr 3d and Hf 4f orbitals of Hf\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) films after FGA at 300 and 600 °C when the Hf\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) sample was coated with 2 nm-thick Pt film during FGA. The XP spectra of Hf\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) films prior to the annealing treatment are also included. For both spectra, the binding energy peaks shifted to the high energy region after FGA at 300 °C, while the original value was recovered after FGA at 600 °C. The binding energy shift could be attributed to H incorporation. According to Kang et al.\(^{159}\) the complex of VO and H is thermodynamically stable among the various models for H incorporation since H can passivate the dangling bonds due to VO. This shifted the binding energy peaks to the high energy region. In contrast, there is almost no shift of the peaks even after FGA at 300 °C without the capping Pt, suggesting that the Pt top electrode works as a catalyst for H-incorporation. It should be noticed that HfO\(_2\) and ZrO\(_2\) are currently used in the commercialized semiconductor chips (MOSFET and DRAM capacitor) where hydrogen annealing is essentially utilized.
The annealing in a hydrogen atmosphere is more critical for metal/ferroelectric/semiconductor stacks since it is crucial to decrease the interfacial trap density at the ferroelectric/semiconductor interface. Oh et al.\textsuperscript{160} studied the effects of high-pressure hydrogen annealing on the ferroelectric properties of W/Al:HfO\textsubscript{2}/W and W/Al:HfO\textsubscript{2}/Si capacitors, and reported that the endurance of the W/Al:HfO\textsubscript{2}/Si capacitor could be improved by decreasing the interfacial trap density. From TEM analysis, the 1.5 nm-thick interfacial layer at the Al: HfO\textsubscript{2}/Si interface could be observed. After high-pressure hydrogen annealing at 10 atm for 30 minutes at a temperature of 300 °C, $P_t$ decreased by up to 66% suggesting the incorporation of H and subsequent pinning of polar dipoles in Al: HfO\textsubscript{2}. After wake-up field cycling, however, the $P_t$ of the hydrogen annealed sample could recover to $\sim$84% of the Al:HfO\textsubscript{2} capacitor without hydrogen annealing. The endurance of the W/Al:HfO\textsubscript{2}/Si capacitor could be improved from $10^5$ to $10^9$ times through high-pressure hydrogen annealing. This result implies that the hydrogen ions incorporated in ferroelectric HfO\textsubscript{2} may be mobile, and their drift and redistribution may occur during wake-up field cycling similar to that of VO\textsubscript{2}.

The H atoms and protons in ferroelectric HfO\textsubscript{2} films can be a byproduct of the ALD process, especially when the metal–organic precursors and/or oxygen source with H (such as H\textsubscript{2}O and H\textsubscript{2}O\textsubscript{2}) are utilized. Kim et al.\textsuperscript{161} compared the chemical and electrical properties of ALD Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} thin films deposited utilizing O\textsubscript{3} and H\textsubscript{2}O as oxygen sources. From $P$–$V$ curves, the Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} thin films deposited using O\textsubscript{3} could show larger $P_t$ and $V_c$ compared to films deposited using H\textsubscript{2}O. To understand the differences, they initially considered different concentrations of residual C and VO as potential causes. However, the chemical analysis and electrical characterization did not show notable differences in the concentrations of residual C and VO. From SIMS, Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} thin films deposited using H\textsubscript{2}O showed higher H concentration compared to the other film. Since the difference in residual C concentration for the two cases was negligible, they concluded that the H ions originated from H\textsubscript{2}O.

The H in ferroelectric doped HfO\textsubscript{2} can also affect the internal field formation and electrical conduction mechanism. Park et al.\textsuperscript{162} examined the effect of the annealing atmosphere (N\textsubscript{2}, O\textsubscript{2}, and forming gas) on the chemical and ferroelectric properties of Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} thin films. It could be confirmed that the internal field was influenced by the annealing atmosphere, possibly due to the difference in the distribution of V\textsubscript{O} at the Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2}/TiN interface. When the TiN/Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2}/TiN capacitor was annealed in forming gas (95% N\textsubscript{2} + 5% H\textsubscript{2}), the shift of the $P$–$E$ curve due to V\textsubscript{O} formation could be observed. They also examined the conduction mechanism of TiN/Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2}/TiN capacitors by considering various conduction mechanisms, and the conduction by Poole–Frenkel emission, which is governed by the thermal conduction between trap sites in the film bulk region, could be confirmed. The trap level estimated from the temperature-dependent examination was $\sim$0.2 eV below the conduction band minimum, which could be ascribed to interstitial H.

In summary, the incorporation of H atoms into doped-HfO\textsubscript{2} based ferroelectric films degraded the performance which was shown to be more severe when thin Pt capping electrodes were deposited. However, the degree of degradation was much lower compared with the perovskite ferroelectrics, perhaps due to the higher binding energy of the constituent cations (Hf and Zr) to oxygen ions compared with the counterparts of the perovskite ferroelectrics. As the forming gas annealing is an indispensable process in Si-chip fabrication, careful examination of the effect of H at the oxide/semiconductor interfaces, oxide/metal interfaces or oxide bulk on the ferroelectric performance of the HfO\textsubscript{2}-based film, both in the capacitor and FET configurations, is crucial. Nonetheless, the possible influence of H atoms on the evolution of the ferroelectric phase has not been studied in detail to date.

Nitrogen

Nitrogen is also an important defect that can affect the ferroelectric and electrical properties of fluorite-structure oxides. For the cases of ferroelectric doped HfO\textsubscript{2} or Hf\textsubscript{1−x}Zr\textsubscript{x}O\textsubscript{2} thin films grown by the ALD method, residual N impurities can originate from the organic ligands of metal–organic precursors. Especially, TEMA-M and TDMA-M (M: Hf or Zr) precursors, which are the most frequently used metal–organic precursors, contain N atoms in their ligand. It was reported that the residual N concentration is sensitively affected by the growth temperature.\textsuperscript{163} Moreover, the metal nitrides such as TiN and TaN are the most frequently used electrode materials for ferroelectric doped HfO\textsubscript{2} or Hf\textsubscript{1−x}Zr\textsubscript{x}O\textsubscript{2} thin films. When high-temperature annealing by the RTP for crystallization is conducted, the diffusion of N from the metal nitride electrode into the oxide films is highly probable. The diffusion of N was experimentally confirmed in the previous works.\textsuperscript{144,165}

In the computational simulations, N was regarded as a dopant substituting oxygen in the ferroelectric Pbca\textsubscript{1} orthorhombic phase.\textsuperscript{146} The N atoms could have been incorporated at the interstitial sites, which is yet to be studied in the Pbca\textsubscript{2} orthorhombic phase. Among oxygen sites with three (O3) and four (O4) neighboring Hf ions, substitution of O3 by N decreases the free energy difference between the ferroelectric orthorhombic phase and the monoclinic phase by a larger magnitude ($\sim$20 meV per f.u. @3.125% doping) than the substitution of O4 sites [less than 0.2 meV@3.125% doping].\textsuperscript{146} Fig. 7a and b show the free energy values of the various crystalline phases when N substituted O3 and O4 sites, respectively.\textsuperscript{146} Zhou et al. reported that the effect of N doping on the free energy difference between the ferroelectric orthorhombic and monoclinic phase was even larger than that caused by La doping with equivalent concentration.\textsuperscript{146} It should be noted that La is one of the dopants which can significantly decrease the free energy of the ferroelectric orthorhombic phase\textsuperscript{41} and that the large $P_t$ (>$25 \mu$C cm$^{-2}$) was experimentally confirmed. From the computational simulation, therefore, N is expected to influence the Pbca\textsubscript{2} orthorhombic phase formation and the resulting ferroelectric properties of HfO\textsubscript{2} thin films.

From the experiments, N was reported to induce ferroelectricity in physical vapor deposited HfO\textsubscript{2} thin films, and it
B28 nm-thick 0.34% N-doped HfO2 film with a field-effect-transistor is yet to be studied. The electrical properties of the metal–ferroelectric–semiconductor effect of N related defects on the trap levels and the resulting fixed charge in the metal–oxide–semiconductor field-effect-transistors.166 In the phase diagrams of bulk HfO2 and ZrO2, the Pca21 orthorhombic phase cannot be stabilized. However, in the experiments, the ferroelectric orthorhombic phase can be formed by several deposition techniques using various dopants. Therefore, the surface energy effect was suggested as key to understanding the unexpected ferroelectricity in doped HfO2. The pioneering computational simulation work by Materlik et al.44 is important in this regard. In that work, they suggested that both bulk free energy and surface free energy of the ferroelectric orthorhombic phase are between those of the tetragonal and monoclinic phases. It should be noted that the free surface of fluorite-structure ferroelectrics is not involved in the practical electronic devices, such as metal–ferroelectric–metal capacitors or ferroelectric field-effect-transistors, utilized for electrical characterization. Instead, interfaces between different fluorite-structure ferroelectrics and metals or semiconductors and grain boundaries existing in fluorite-structure ferroelectrics are practically more important than the free surface. The orthorhombic phase stabilization due to the surface energy effect was discussed in detail in other reviews or research papers.44–49

Besides the aforementioned size effect, the ferroelectric properties are strongly influenced by a chemically distinguishable interfacial non-ferroelectric layer and grain boundaries. The chemically distinguishable interfaces are generally originating from the oxidation of metal electrodes or semiconductor surfaces. Especially severe effects were observed when the ferroelectric HfO2 directly contacts the Si substrate, which is part of the gate stack in the FeFET. Another important 2D defect is the non-ferroelectric second phase at the electrode/ferroelectric interfaces. Such interface has been suggested as a key factor that can deteriorate the ferroelectric properties in the pristine state, resulting in the so-called “wake-up” effect. The other issue is grain boundaries, on which the mobile V0 can accumulate due to the grain boundary-defect attraction. Such accumulation resulted in limited endurance due to the formation of permanent conduction paths. In this section, therefore, other aspects such as oxidized interfacial layer, interfacial non-ferroelectric 2nd phase, and grain boundary will be discussed.

The oxidation of the Si substrate has been a critical issue for both state-of-the-art MOSFETs with HfO2 gate insulators and FeFETs with conventional ferroelectric oxides. It should be noted that HfO2-based FeFETs suffer less from the low-k SiO2
interfacial formation than FeFETs with conventional ferroelectrics. This difference comes from the differences in the dielectric constant of ferroelectric HfO$_2$ (25–30) and conventional perovskite-structure oxides (generally a few hundreds in thin films). The dielectric constant of SiO$_2$ is only 3.9, and the dielectric constant is inversely proportional to the electric field across the serially connected dielectric films. Therefore, the electric field across SiO$_2$ is ~7.2 and 77 times higher than that across ferroelectric HfO$_2$ and Pb(Zr,Ti)O$_3$ (k ~ 300), respectively. Although the situation in ferroelectric HfO$_2$ seems much better compared to that in PZT, it can still be a serious issue for low power device performance. When a gate bias is applied across the gate stack of a FeFET, a significant portion of the field is applied across the SiO$_2$ interfacial layer, which increases the minimum voltage required to program and erase processes. The increase in the operation voltage of FeFETs results in high power consumption.

Another issue originating from the dielectric constant difference between interfacial SiO$_2$ and ferroelectric thin films is the limited retention due to the depolarization fields. When an interfacial non-ferroelectric layer exists between the ferroelectric layer and the electrode or semiconductor channel, an electric depolarization field is formed in the ferroelectric layer. As a result, the memory window of the FeFET can decrease with increasing time when the depolarization field is not negligible. Gong and Ma$^{164}$ explained why the retention of ferroelectric HfO$_2$-based FeFETs is superior to that of conventional ferroelectrics such as PZT or SBT due to their lower dielectric constant and higher coercive field, and it will be reviewed in detail below.

The depolarization field can be calculated using eqn (1) below:

$$E_{\text{dep}} = P[(\varepsilon_{\text{FE}} \varepsilon_0 d_{\text{FE}}/\varepsilon_{\text{IL}} d_{\text{IL}} + 1)]^{-1}$$  \hspace{1cm} (1)

Here, $E_{\text{dep}}$, $P$, $\varepsilon_{\text{IL}}$, $\varepsilon_0$, $d_{\text{FE}}$, and $d_{\text{IL}}$ refer to the depolarization field, ferroelectric polarization, dielectric constant of the ferroelectric, dielectric constant of the interfacial layer, vacuum permittivity, the thickness of the ferroelectric, and the thickness of the interfacial layer, respectively. From eqn (1), it can be noticed that the ferroelectric with a lower $\varepsilon_{\text{FE}}$ is beneficial for having a lower depolarization field for a given thickness and dielectric constant of the interfacial layer. Therefore, ferroelectric HfO$_2$ ($\varepsilon_{\text{FE}}$ ~ 30) is expected to have $E_{\text{dep}}$ ~1 order of magnitude lower compared to PZT ($\varepsilon_{\text{FE}}$ ~ 300 in thin films) when the other parameters in eqn (1) are fixed. Buragohain$^{165}$ et al. compared depolarization field trends for both material systems.

Another important factor is the coercive field; from experimental observations in the literature, it is generally accepted that the $E_c$ of ferroelectric HfO$_2$ is higher than that of conventional ferroelectrics such as PZT and SBT by ~1 order of magnitude. Toriumi$^{167}$ et al. relate the magnitude of the coercive field to the inverse of the dielectric constant as expected from Landau theory. In addition, the depolarization field should be strongly related to the relative ratio of $E_{\text{dep}}$ to $E_c$. Thus, when the difference in $E_c$ is considered together with the difference in the depolarization field discussed above, the expected improvement of the retention becomes even higher. In Gong and Ma’s paper,$^{164}$ the $E_{\text{dep}}/E_c$ value of ferroelectric HfO$_2$ (~2) was much smaller than that of PZT (~17) and SBT (7), when the film thickness is 10 nm.

The voltage drop across the non-ferroelectric interfacial layer and depolarization field issues are also expected at the metal/ferroelectric interfaces. However, in this case, the magnitude of the voltage drop and depolarization field is much smaller compared to that at the ferroelectric/SiO$_2$/Si interface. It has been suggested that the interfacial non-ferroelectric phase near the electrodes is most likely the tetragonal phase whose dielectric constant is ~40.$^{40,44}$ Therefore, when the thickness of the interfacial layer is the same, the voltage drop and depolarization field resulting from the 1 nm-thick tetragonal phase layer is ~1 order of magnitude lower than that of SiO$_2$ with equivalent thickness.

Because the interfacial layer can have a much higher defect density, charge trapping at the interfacial layer can represent a critical issue. Ali et al.$^{168}$ compared the retention properties of Si:HfO$_2$ based FeFETs with the SiO$_2$ and SiON interfacial layer between Si:HfO$_2$ and Si. From the extrapolation of the accelerated retention test at 150 °C, the memory window values expected after 10 years were 0.15 and 0.5 V for the SiO$_2$ and SiON interfacial layers, respectively, whereas the initial memory window values were 0.75 and 0.95 V. They concluded that the improved charge trapping is the main reason for the enhanced retention of the FeFET with the SiON interfacial layer rather than the difference in the $k$ value.

From the discussions above, the interfacial layer is expected to be critical for the electrical properties of ferroelectric HfO$_2$-based devices. Several important works on this topic are reviewed in this section.

Lomenzo et al.$^{169}$ examined the effect of an interfacial low-$k$ non-ferroelectric layer by inserting an Al$_2$O$_3$ ($k$ ~ 9) layer with various film thicknesses between TiN and Hf$_{0.5}$Zr$_{0.5}$O$_2$ films. They showed that for a given pulse height, the $P_r$ value significantly decreases with increasing Al$_2$O$_3$ thickness due to the increased voltage drop across the Al$_2$O$_3$ layer. By using eqn (1), they also calculated the depolarization field, and found that it increased with increasing Al$_2$O$_3$ thickness from 0 to 1.5 nm. Due to the increased depolarization field, the retention performance was also degraded.

Park et al.$^{170}$ examined the ferroelectric properties of TiN/ Hf$_{0.5}$Zr$_{0.5}$O$_2$/TiN capacitors with Hf$_{0.5}$Zr$_{0.5}$O$_2$ films thinner than 8 nm. After the wake-up field cycling of $10^5$ times, the thickness of the non-ferroelectric interfacial layer was negligible. They reported that the coercive field decreased with decreasing film thickness due to the increased depolarization field. Their observation could be quantitatively explained by Dawber’s model,$^{171}$ which considers the depolarization field due to the finite screening length in electrodes. From the changes in the coercive field with varying film thickness, the intrinsic coercive field was calculated as ~1.43 MV cm$^{-1}$, which is higher than the experimentally observed coercive field.

On the other hand, the opposite trend, i.e., an increase in the coercive field with the decrease in film thickness, was reported by Mimura et al.$^{172}$ in their epitaxial Y:HfO$_2$ film...
deposited on the ITO/YSZ substrate. Understanding the thickness effect in ferroelectric HfO₂ thin films is highly challenging since it could be also affected by other factors such as polymorphism and strain, rather than the size effect being driven exclusively from the ferroelectric properties. This topic, thus, requires further study.

The formation of the defective SiO₂ interfacial layer at the Si/HfO₂ interface is a critical issue for the scaling down of MOSFETs with high-k dielectric HfO₂. Kim et al. reported that the formation of a SiO₂ interfacial layer could be suppressed by depositing a scavenging Ti layer on HfO₂ and ZrO₂ in the metal/oxide/Si gate stack of MOSFETs. Due to the suppressed interfacial layer growth, the equivalent oxide thickness in the MOSFET could even be decreased for further scaled devices. Given the similarity of MOSFET and FEFET gate stacks, the scavenging effect can also be applied to the HfO₂-based FeFETs.

For this purpose, Lomenzo et al. comparatively studied the ferroelectric properties of TaN/HfO₂/TaN, TaN/HfO₂/Ge, and TaN/HfO₂/Ge₂, and found that the TaN/HfO₂/Ge capacitor showed a Pₘ value larger than that of TaN/HfO₂/Ge with better endurance. This result was impressive since it is generally known that optimizing Ge-based devices is much more complicated than optimizing Si-based devices due to the lower stability of GeO₂ compared to SiO₂. When the HfO₂/Ge and HfO₂/Ge interfaces were compared, no interfacial layer was formed on Ge, whereas a 1.5 nm-thick interfacial layer was formed on Si. In this study, the reason for such difference was not discussed. However, the difference can be understood based on the scavenging effect by the TaN electrode. The formation free energy of GeO₂ is much smaller than that of SiO₂, suggesting that the top TaN electrode can more easily scavenge oxygen atoms from GeO₂.

From the viewpoint of the scavenging effect, the elemental semiconductors with lower oxide formation energy or oxide semiconductors might be beneficial to suppress the interfacial layer growth. For the Si channel FeFETs, the utilization of the scavenging effect could be crucial to suppress the interfacial layer growth and fabricate FeFETs with low operation voltage, sufficient retention, and improved endurance.

To summarize, the interfacial non-ferroelectric phase is a critical defect that can directly affect the operation voltage and retention of the electronic devices based on fluorite-structure ferroelectrics. To mitigate the non-ferroelectric interfacial layer formation, redox reactions at the ferroelectric/semiconductor or ferroelectric/metal interfaces should be understood. This topic was intensively studied in MOSFETs when HfO₂ was introduced as a high-k material replacing SiO₂. Utilizing the scavenging effect is therefore suggested as one promising strategy in this review for future device development employing HfO₂-based ferroelectrics.

Grain boundaries

The grain boundary is also a 2D defect which can significantly influence the electric properties of ferroelectric HfO₂. The strong interaction between grain boundaries and point defects or line defects has been a critical topic in materials science. It was suggested that the grain boundary energy might affect the polymorphism thermodynamically and kinetically. This topic was reviewed in another progress report on ferroelectric phase formation in HfO₂-based ferroelectrics. In this section, the effect of grain boundaries on carrier conduction, contribution to the leakage current, and subsequent reliability performance degradation are reviewed based on previous studies on resistive switching oxides.

The electric field required for resistive switching (∼MV cm⁻¹ level) is similar to that needed for ferroelectric switching. Starschich et al. experimentally proved that resistive switching and ferroelectric switching could be concurrently observed in chemical solution deposited ferroelectric Y:HfO₂ thin films. After the pre-treatment for the electroforming process utilizing 3.6 MV cm⁻¹-high and 10 s-long triangular pulses, resistive switching could be observed. The phenomenon is regulated by a valence change mechanism originating from the drift/accumulation/percolation of VO's. Besides the electroforming process, a reliable ferroelectric switching could be observed in the same sample with a gradual increase of switchable polarization with the increasing number of switching cycles (wake-up). Max et al. reported that the reset behavior can be changed to a “deep reset” after ferroelectric field cycling making it possible to repeat ferroelectric switching even after the resistive switching was performed. These reports provide an important hint on the critical role of VO in both resistive switching and wake-up.

Pesic et al. studied the evolution of chemical and ferroelectric properties of ferroelectric HfO₂ during field cycling tests. The wake-up effect is associated with a redistribution of VO's rather than an increase in their number. The decrease in VO concentration at the interfacial region results in a decrease in domain pinning site concentration. It also resulted in the phase transition from the non-ferroelectric tetragonal or monoclinic phase to the ferroelectric orthorhombic phase. During the fatigue stage, the overall VO concentration increased with the increasing number of polarization switching cycles, causing an increase in domain pinning and, therefore, a decrease of the switchable polarization. Eventually, the accumulation of VO forming the permanent filament connecting the top and bottom electrodes can result in the hard breakdown, which has been frequently observed in ferroelectric HfO₂ systems.

For the permanent conducting filament formation in oxide materials, defective sites for oxygen vacancy accumulation are generally preferred. Grain boundaries have been suggested as a preferable site for this phenomenon to occur. Moreover, the grain boundary connecting the top and bottom electrodes within the columnar grain structure is expected to contribute to carrier conduction. In previous studies on the conduction mechanism of HfO₂-based thin films, grain boundaries were suggested as trap sites with rather shallow trap depths (<0.5 eV), which can contribute to trap assisted tunneling or Poole–Frenkel emission. For the same reason, amorphous HfO₂ without grain boundary was preferred for the gate oxide in MOSFETs, and a rather complicated ZrO₂/Al₂O₃/ZrO₂ trilayer stack, in which Al₂O₃ is intervening the columnar grain boundary, has been utilized in DRAM capacitors.
Grain boundaries were reported to significantly affect the dielectric relaxation as well as the conduction of charge carriers in perovskite-structure ferroelectrics.\textsuperscript{181–184} It was reported that the long-range motion of doubly ionized oxygen vacancies could contribute to the electrical conduction under DC bias, while their short-range hopping could contribute to the dielectric relaxation.\textsuperscript{181–184} Schenk et al.\textsuperscript{184} studied the impedance spectra of TiN/Si:HfO\textsubscript{2}/TiN capacitors, and showed that the parallel connection of grains and grain boundaries is a critical difference of ultra-thin fluorite-structure ferroelectrics with columnar grain structure compared to bulk ceramics. They suggested that the contribution of interfacial layers and grain boundaries becomes more significant with decreasing film thickness and lateral grain size.\textsuperscript{184}

Grain size is even more critical for scaled devices used in high-density memory arrays. For the large-scale capacitors within \(10^2\)-\(mm\textsuperscript{3}\) scale, non-uniformity induced by grain size has not been considered as a critical issue, because \(~10^4\) grains are included in one memory device. The averaged ferroelectric properties of more than \(10^4\) grains are experimentally measured, and statistical non-uniformity in device performance is negligible. However, for the practically scaled devices with sub \(30 \text{nm}\) feature size, the situation is starkly different. When the lateral grain size is assumed to be comparable to film thickness, the scaled devices would have several grains with grain boundaries between them. Generally, ferroelectric HfO\textsubscript{2} films grown by an ALD process have a randomly oriented texture, meaning the ferroelectric properties of the nearby grains in a device are expected to be different from each other. As a consequence, non-uniform ferroelectric switching in the unit devices and statistically non-uniform performance in the integrated systems are expected. Mulaosmanovic et al.\textsuperscript{185} experimentally observed step-like multi-level switching in FeFETs with \(30 \text{nm}\) channel length, which could be attributed to the grain-by-grain switching for three grains with different coercive fields. Fig. 9a-c show the schematic diagram of FeFETs with three nanoscale grains of ferroelectric Si:HfO\textsubscript{2}, the cross-sectional TEM image of the fabricated FeFET with \(30 \text{nm}\) channel length, and drain current–gate voltage (\(I_D\)-\(V_G\)) curves of the FeFET. Fig. 9d shows the \(I_D\)-\(V_G\) transfer characteristics of a \(30 \text{nm}\) long device after a positive and a negative gate pulse, which correspond to down polarization (red curve) and up polarization (blue curve) of all ferroelectric domains present, respectively. Fig. 9e shows the \(I_D\)-\(V_G\) read-out curves after each of the progressively increasing \(V_p\) pulses in the inset. Fig. 9f shows drain current from Fig. 9e, extracted for the sake of clarity at a gate voltage of \(0.36 \text{V}\) vs. the corresponding \(V_p\), showing four different current levels. (g) Threshold voltage extracted from (e), vs. the corresponding \(V_p\). Three discrete and abrupt \(V_p\) shifts correspond to separate switching of three domains within the stack (inset). Panels b, c, and d–g refer to three different devices, respectively. Reproduced in part with permission from ref. 185. Copyright 2017 American Chemical Society.

To summarize, the grain boundary in fluorite-structure ferroelectrics can serve as a defect site for oxygen vacancy accumulation which causes the permanent leakage path formation and the consequent hard-breakdown leading to device failure. Moreover, the nanoscale grain size resulted in inhomogeneity of the high-density array of ferroelectric memories. In fluorite-structure ferroelectrics with practical film thicknesses of \(10 \text{nm}\) or even smaller, the grain boundary of the columnar grain structure connects the top and bottom electrodes contributing to conduction of charge carriers. Thus, decreasing the areal ratio of the grain boundary by increasing grain size can be a strategy (1) to improve endurance, (2) to improve spatial uniformity of ferroelectricity, (3) and to decrease leakage current.

**Conclusions**

The effects of various point defects and 2D defects on the ferroelectric properties of fluorite-structure oxides have been reviewed. In contrast to conventional ferroelectrics, ferroelectric HfO\textsubscript{2} could be aggressively scaled down using mature fabrication processes. The scalability of ferroelectric HfO\textsubscript{2} has revealed critical effects from defects, which have not been considered as essential in large scale devices. Furthermore, the high coercive field of ferroelectric HfO\textsubscript{2} is sufficient to drift charged defects such as oxygen vacancies during switching. The intricate polymorphism originating from small energy
differences between the competing crystalline phases makes the situation even more complicated.

Fortunately, there have been numerous previous studies on MOSFETs with HfO₂ gate insulator and resistive switching in HfO₂ or ZrO₂ films. Those previous works provide the ferroelectric community with hints for setting strategies to overcome the above-mentioned obstacles for practical device applications.

Oxygen vacancies might be the most critical point defects in ferroelectric HfO₂ with a significant effect on competition between various crystalline phases, dynamic phase transition during repetitive polarization switching, and hard breakdown due to the formation of permanent conduction paths. Currently, the primary origin of oxygen vacancies is believed to be the partial reduction of ferroelectric HfO₂ due to the scavenging effect of the adjacent electrodes, such as TiN. In this regard, exploiting another electrode material with lower oxygen scavenging properties could be critical. However, at the same time, the influence of the new electrode on the formation of the desired ferroelectric phase and its CMOS-process-integrability, such as mature deposition and etching process, should be taken into consideration.

Residual C impurities can be formed from the organic ligands of metal–organic precursors, which are most frequently used in the ALD of ferroelectric HfO₂. An increase in C impurities also decreases the free energy difference of metastable phases and consequently affects the polymorphism in ferroelectric HfO₂. Nonetheless, a very high C concentration adversely interferes with the ferroelectric phase formation (prefers tetragonal phase) and degrades the reliability by forming trap sites which increase the leakage current. Thus, to decrease the residual C concentration, understanding chemical reactions between metal precursors, oxygen sources, and the substrate or previously deposited film is required. Since HfO₂ and ZrO₂ are currently used for mass production of commercial memory devices, controlling C impurities should be possible with the existing knowledge.

H can originate from metal precursors as well as from the annealing atmosphere. The latter mechanism is believed to be more critical since hydrogen annealing is an important process to optimize the oxide/semiconductor interfaces and decrease the trap density. H impurities are incorporated at the interstitial positions of ferroelectric HfO₂. For this reason, the inner unit cell motion of ions can be critically suppressed, resulting in a drastic decrease in \( P_r \). Moreover, ferroelectric oxides can be reduced by hydrogen resulting in metal-rich phases with high conductivity. Compared to the conventional ferroelectrics such as PZT and SBT, the degradation by H incorporation was much weaker in ferroelectric HfO₂. The Pt top electrode accelerated the H incorporation process by its catalytic activity. Such a phenomenon should be considered when selecting the electrode material for ferroelectric HfO₂. From a recent study by Oh et al., it was suggested that H impurities are also mobile under electric pulses similar to oxygen vacancies. The drift/accumulation dynamics of H impurities needs further study.

The interfacial non-ferroelectric layer formation, especially at the ferroelectric HfO₂/semiconductor interface, is another critical issue when low power consumption and high reliability are targeted. The undesired voltage drop across the interfacial layer increases the total program/erase voltage and the resulting power consumption of the system. Moreover, the depolarization field by the physical separation of polarization and compensating charges in electrodes deteriorates the retention of the stored polarization states. Finally, the high defect concentration in the interfacial layer increases charge trapping and affects the device parameters, such as the threshold voltage. Thus, the interfacial SiO₂ formation is a crucial issue to be resolved to achieve highly reliable FeFETs. The scavenging effect intensively studied for scaling down of HfO₂-based MOSFETs is expected to be applied in HfO₂-based FeFETs. The unexpectedly high interface quality of the HfO₂/Ge interface might originate from the scavenging effect of the less stable GeO₂. Ge channel FeFETs with HfO₂ ferroelectrics are thus considered as promising devices.

The grain boundaries also affect the polymorphism and electrical properties of HfO₂. Grain boundaries have been reported as the accumulation sites for charged defects such as oxygen vacancies. In ferroelectric HfO₂, accumulation of oxygen vacancies at grain boundaries and subsequent permanent conducting path formation could lead to a hard breakdown. Furthermore, grain boundaries contribute to the conduction of electrons \( \text{via} \) trap assisted tunneling or Poole–Frenkel emission by working as shallow trap sites. Last but not least, the statistical non-uniformity in the ferroelectric properties of individual grains can be a critical issue for the practically scaled devices. Thus, increasing grain size and decreasing relative fraction of the grain boundary is believed to be promising for ferroelectric memories with low power consumption and high reliability. However, increasing grain size may further aggravate the non-uniformity issue of the nano-scale devices. In this case, a much finer grain size would be necessary, but that also requires substantial improvement in the grain boundary property which may be highly challenging.

Although the research on ferroelectricity in HfO₂ and ZrO₂ has a history shorter than ten years to date, the knowledge and technology on ferroelectric HfO₂ are rapidly advancing based on the foundation set in previous studies on non-ferroelectric HfO₂ for memory devices, as well as conventional ferroelectrics with different crystalline structures, although many technical obstacles are still to be overcome. This review is expected to shed light on the less focused defect chemistry of fluorite-structure ferroelectrics and to contribute to a better understanding of these emerging ferroelectric materials.

The role of defects in conventional ferroelectric materials including perovskite-structure oxides has been intensively studied, and, in principle, the roles of defects in fluorite-structure ferroelectrics are physically similar. However, the small film thickness and lateral grain size, which have not been achieved with the conventional ferroelectrics, of the fluorite-structure ferroelectrics enhance the effect of defects. Moreover, the higher operational field due to the high \( E_c \) values of \( \sim 1–2 \text{ MV cm}^{-1} \) enables a drift of mobile charged defects such as oxygen vacancies, which affects nanoscale polymorphism. Based on the previous studies on MOSFETs and cell capacitors of DRAMs,
which contain fluorite-structure oxides as the key materials, it is expected that the defect-related issues can be solved for the next-generation scaled electronic devices with fluorite-structure ferroelectrics.

Conflicts of interest

There are no conflicts to declare.

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