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|  | PAPER | **[View Article Online](http://dx.doi.org/10.1039/C7TC01200D)** | | | | |
| **[View Journal](http://pubs.rsc.org/en/journals/journal/TC)  [| View Issue](http://pubs.rsc.org/en/journals/journal/TC?issueid=TC005019)** | | | | |
| Published on 19 April 2017. Downloaded by Georgia Institute of Technology on 17/04/2018 06:05:05. |  | A comprehensive study on the structural | | | | |
| evolution of HfO2 thin films doped with various dopants† | | | | |
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| 5, 4677 |
| Received 21st March 2017, | M. H. Park, |  | \*aT. Schenk,aC. M. Fancher, | | b E. D. Grimley,c C. Zhou,d C. Richter,a  ae and U. Schroedera |
| J. M. LeBeau,cJ. L. Jones,cT. Mikolajick | | |  |
| The origin of the unexpected ferroelectricity in doped HfO2 thin films is now considered to be the | | | | |
| formation of a non-centrosymmetric Pca21 orthorhombic phase. Due to the polycrystalline nature of the | | | | |
| films as well as their extremely small thickness (B10 nm) and mixed orientation and phase composition, | | | | |
| structural analysis of doped HfO2 thin films remains a challenging task. As a further complication, | | | | |
| the structural similarities of the orthorhombic and tetragonal phase are difficult to distinguish by typical | | | | |
| structural analysis techniques such as X-ray diffraction. To resolve this issue, the changes in the grazing | | | | |
| incidence X-ray diffraction (GIXRD) patterns of HfO2 films doped with Si, Al, and Gd are systematically | | | | |
| examined. For all dopants, the shift of o111/t101 diffraction peak is observed with increasing atomic layer | | | | |
| deposition (ALD) cycle ratio, and this shift is thought to originate from the orthorhombic to P42/nmc | | | | |
| tetragonal phase transition with decreasing aspect ratio (2a/(b + c) for orthorhombic and c/a for the | | | | |
| tetragonal phase). For quantitative phase analysis, Rietveld refinement is applied to the GIXRD patterns. | | | | |
| A progressive phase transition from P21/c monoclinic to orthorhombic to tetragonal is confirmed for all | | | | |
| dopants, and a strong relationship between orthorhombic phase fraction and remanent polarization | | | | |
| Accepted 19th April 2017 | value is uniquely demonstrated. The concentration range for the ferroelectric properties was the | | | | |
| DOI: 10.1039/c7tc01200d | narrowest for the Si-doped HfO2 films. The dopant size is believed to strongly affect the concentration | | | | |
| [rsc.li/materials-c](http://rsc.li/materials-c) | range for the ferroelectric phase stabilization, since small dopants can strongly decrease the free energy | | | | |
| of the tetragonal phase due to their shorter metal–oxygen bonds. | | | | |
| Introduction | HfO2 and ZrO2 as well as pure ZrO2 21–23 have been intensively  studied by numerous researchers.13The origin of the unexpected | | | | |

Since the first report on ferroelectricity in Si doped HfO2 in 2011,1ferroelectricity in pure HfO2,2–4HfO2 doped with various dopants,5–13and solid solutions14–17or nanolaminates18–20of

ferroelectric properties is now believed to be the formation of the non-centrosymmetric orthorhombic phase (space group Pca21, No. 29).1,25,26It should be noted that this orthorhombic phase is

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| a NaMLab gGmbH, Noethnitzer Str. 64, 01187 Dresden, Germany.  E-mail: MinHyuk.Park@namlab.com  b Neutron Scattering Science Directorate, Oak Ridge National Laboratory,  Oak Ridge, Tennessee 37831, USA  c Department of Materials Science and Engineering, North Carolina State University, | different from the centrosymmetric orthorhombic phases which are previously known as high pressure phases of bulk HfO2 and ZrO2.27,28Although this non-centrosymmetric phase was reported before by both experimental and theoretical works, its ferroelectricity was not checked at the time.27,28The ferroelectric |

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and field-induced ferroelectric properties of HfO2-based films are considered promising for various applications including non-volatile memories, negative capacitance field-effect-transistors, energy storage/harvesting, and solid-state cooling, based on its properties that distinguish it from conventional ferroelectrics

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| ment retains and the publisher, by accepting the article for publication, acknowl- | based | mostly | on | the | perovskite | or | layered | perovskite |

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structures.9,24,29–35Above all, HfO2 itself is highly scalable and Si-compatible, and it has been used in the semiconductor industry since its first adoption by Intel.36As ferroelectrics have been downscaled for use in devices, a so-called ‘‘size effect’’appeared which limits, or eliminates entirely, functional

*J. Mater. Chem. C,* 2017, 5, 4677--4690 | 4677

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properties at ultra-thin thicknesses. This has been a critical problem for downscaling of conventional ferroelectrics.37In

contrast, ferroelectric properties with remanent polarizations (Pr) larger than 15 mC cm�2are confirmed for doped HfO2 films that are 10 nm-thick or even thinner. This has enabled

the fabrication of the first 28 nm ferroelectric gate field-effect transistors (FeFET).9,24,29,30According to the extrapolated

Though considerable steps towards epitaxial and/or highly textured HfO2 films have been reported recently,41,45,46polycrystal-line films are relevant for device application and thus require an adequate structural analysis. Despite the aforementioned difficul-ties with X-ray techniques and this material, macroscopic struc-tural analysis via GIXRD is one of the most useful approaches to understand the structural evolution in doped HfO2-based films. In

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| Published on 19 April 2017. Downloaded by Georgia Institute of Technology on 17/04/2018 06:05:05. | retention test, the two memory states are expected to remain | this study, therefore, the macroscopic and microscopic structural |
| for 10 years, and these FeFETs are believed to be superior to | properties are systematically examined using GIXRD, and the |
| those prepared with conventional ferroelectrics based on the | obtained results are discussed in the context of the STEM results. |
| perovskite structure.9,24,29,30,38Theoretical work from Ma et al. | Experimental |
| suggests that the ferroelectric doped HfO2 films have longer |
| retention because of their relatively low relative permittivity er |
| and their high coercive field compared to those of conventional | Sample preparation |
| ferroelectrics.39 |
| The doped HfO2 films were deposited using a thermal ALD |
| Despite the fact that the promising ferroelectric properties |
| process on TiN electrodes on p-type 100 Si substrates. The TiN |
| of doped HfO2 films have been confirmed by intense research, |
| bottom electrode was deposited via reactive magnetron sputter- |
| the dependence of structure on dopant concentration remains |
| ing at room temperature using a Ti target within an N2 atmo- |
| to be systematically characterized. Starschich et al. comprehen- |
| sphere for Si- and Al-doped HfO2 films, and via plasma enhanced |
| sively examined the effect of dopant species on ferroelectric |
| properties of chemical solution deposited (CSD) HfO2 films,11 | ALD for Gd-doped HfO2 films. For the deposition of Si-doped |
| HfO2 films, tetrakis(ethylmethylamino)hafnium (TEMAHf) and |
| but there are critical differences between CSD and ALD HfO2 |
| N,N,N0,N0 0-tetraethyl silanediamine (SAM.24) were used as pre- |
| films. From Grazing incidence X-ray diffraction (GIXRD) pat- |
| terns of CSD HfO2 films, the dominant crystalline phase is | cursors, and H2O and O2 plasma were used as oxygen sources, |
| respectively. The Si dopant concentration within films could be |
| believed to be cubic phase, and their Pr values before wake-up |
| controlled by changing the HfO2 : SiO2 ALD cycle ratio. For the |
| field cycling were quite small.11After wake-up field cycling, |
| however, the CSD HfO2 films could show Pr values as large as | deposition of Al-doped HfO2 films, hafnium tetrachloride (HfCl4) |
| and trimethyl aluminium (TMA) were used as precursors, respec- |
| those of ALD HfO2 films. Therefore, it is believed that the phase |
| tively, and H2O was used as an oxidant both for Hf and Al. The |
| evolution during wake-up field cycling is more critical for CSD |
| deposition temperature was 300 1C. For the deposition of Gd-doped |
| HfO2 films than ALD HfO2 films. Therefore, the ALD HfO2 films |
| HfO2 films, hafnium tetrachloride (HfCl4) and Gd(iPrCp)3 were used |
| are considered to be more appropriate for structural analysis, |
| as precursors, and H2O was used as an oxidant both for Hf and Gd. |
| since they might have more ferroelectric phase before wake-up |
| After deposition of the doped HfO2 films, a top TiN capping layer |
| field cycling than CSD films. |
| was deposited via reactive magnetron sputtering using a Ti target |
| The most serious hindrance for structural analysis may be |
| within an N2 atmosphere, and the post-metallization-annealing |
| the structural similarity between the orthorhombic and tetragonal/ |
| (PMA) process was conducted at 800 1C for 20 s in N2 atmosphere |
| cubic phase, which are believed to be the origin of ferroelectric and |
| field-induced ferroelectric properties, respectively.15,24,25Thus far, | for the crystallization of the films. After the PMA process, Pt |
| electrodes were deposited via e-beam evaporation, and the |
| the identification of a non-centrosymmetric phase (required to |
| Pt electrodes were patterned using a shadow mask. Patterned Pt |
| enable ferroelectricity) in doped HfO2 thin films has been success- |
| top electrodes were used as a hard mask during the subsequent |
| fully conducted only by scanning transmission electron micro- |
| scopy (STEM) based methods,24,40,41rather than by structural | TiN wet etch process using a SC1 solution containing NH4OH, |
| analysis such as XRD.42,43The symmetries of the zone axes are | H2O2, and H2O. |

quite distinct for the Hf positions between the orthorhombic phase and the tetragonal/cubic phase using STEM, but broadening of the diffraction peaks due to the small thickness of the sample makes diffraction (both Bragg–Brentano and grazing incidence) non-ideal for clearly distinguished these phases. According to several calculations and experimental works, there is a very small difference between the lattice parameters of the ferroelectric orthorhombic and tetragonal/cubic phase.25,26Furthermore, poly-crystalline doped HfO2 films are mixtures of multiple orientations, which both weakens peak intensities and further broadens them.44 As a result, a very small film volume is aligned along the direction appropriate for the Bragg–Brentano geometry. In most cases only grazing incidence XRD (GIXRD) patterns have yielded the best results for polycrystalline HfO2 films doped with various dopants.

4678 | *J. Mater. Chem. C,* 2017, 5, 4677--4690

Physical and chemical analyses

X-ray reflectivity (XRR) and GIXRD were carried out using a X-ray diffractometer (D8 Discover, Bruker). For GIXRD, the incidence angle was fixed at 0.451, and the diffraction patterns were analyzed within a 2y range of 15–901. For the quantitative structural analysis, a commercial software for Rietveld refine-ment (TOPAS, Bruker) was used. For the Rietveld refinement, fundamental crystal structures of monoclinic, tetragonal, and orthorhombic HfO2 and cubic TiN taken from Crystallographic Information File (CIF)47were used as input. The crystallographic information was taken from Powder Diffraction File (PDF) card numbers 00-034-0104,4804-005-5597,49and 04-011-882050for monoclinic, orthorhombic, and tetragonal phase HfO2, while

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the PDF number for cubic TiN was 00-038-1420.51The details of PDF used for the phases of HfO2 and TiN can be found in the thesis by Schenk.41For the background fitting, a 5th order Chebychev polynomial combined with 1/x function was used. To consider preferred orientation, the March–Dollase model52,53 was used. The preferred orientation of (111) and (101) were considered for orthorhombic and tetragonal HfO2, respectively.

with a beam current of approximately 80 pA. For high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), the detector inner semi-angle was approxi-mately 77 mrad and the probe semi-convergence angle was 19.6 mrad. The RevSTEM imaging technique was used to remove distortion due to thermal drift14using forty 1024 pixel by 1024 pixel image frames acquired with a dwell time of 2 ms

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| Published on 19 April 2017. Downloaded by Georgia Institute of Technology on 17/04/2018 06:05:05. | Scale factors for all phases were also controlled during the fitting | per pixel and a rotation angle of 901 between each successive |
| process. The role of scale factors is to scale the calculated | image frame. |
| intensities of diffraction patterns, so they should be strongly | Results and discussion |
| related with various external factors including X-ray beam inten- |
| sity and measurement time. One of the fitting parameters named |
| ‘zero error’, which shows the shift of the whole diffraction pattern |
| Origin of ferroelectricity in fluorite structure based |
| due to some external causes, was not automatically controlled for |
| ferroelectrics |
| fitting in this study, since unreasonably large shift could be |
| observed in some refinement results with fitting zero error. Thus, | Fig. 1 summarizes the phase dependence upon various driving |
| this term was fixed at zero. | factors (doping, surface energy, stress. . .) reported in HfO2 thin |
| A ferroelectric tester (TF analyzer 3000, Aixacct systems) was | films. Referring to the figure, a phase change from the mono- |
| used to examine the ferroelectric properties of doped HfO2 | clinic (space group P21/c, No. 14), to the orthorhombic, and |
| films. A triangular double pulse was applied to the top elec- | tetragonal (space group P42/nmc, No. 137) phase is visible for |
| trode while the bottom electrode was connected to virtual | increasing dopant content. The stable phase of bulk HfO2 is |
| ground, and a measurement frequency of 1–10 kHz was used. | the monoclinic phase which is centrosymmetric and thus |
| The Pr values for doped HfO2 films were taken from the | incapable of supporting ferroelectricity. Another important |
| polarization-electric field curves achieved with 3.9–4.0 MV cm�1 | metastable phase in bulk or thin film HfO2 is the tetragonal |
| pulse height. For fair comparison, the Pr values in pristine states | phase, and it is well-known that this metastable phase can be |
| were compared with the structural data. The XRD footprint is | stabilized for various dopants or due to surface/interfacial |
| several cm2large. Such large areas cannot be subjected to field | energy effects.24,26,56,57In 2011, the unexpected ferroelectricity |
| cycling without dielectric break down. | was first reported at the morphotrophic phase boundary of the |
| A TOF SIMS V (ION TOF, Inc. Chestnut Ridge, NY) instru-ment, which was equipped with a Bin m+ (n = 1–5, m = 1, 2) liquid | two phases.1Various factors affecting the formation of the |
| orthorhombic phase have been reported. Materlik et al. |
| metal ion gun, Cs+sputtering gun and electron flood gun to | reported that the large free energy difference between the stable |
| compensate charge, was used for TOF-SIMS analyses. The | monoclinic phase and orthorhombic phase within bulk form |
| orientation of both the Bi and Cs ion columns was fixed at | can be compensated by the difference between the surface or |
| 451 with respect to the sample surface normal. The instrument | interfacial energy of the two phases in a polycrystalline thin |
| vacuum system consists of an analysis chamber and an | film structure.26In addition to size effects, various factors such |
| adjacent load lock for rapid sample loading, and they were | as dopant concentration, the stress/strain in thin films, elec- |

separated by the gate valve. To avoid contamination of the surfaces, the pressure of analysis chamber was maintained below 5.0 � 10�9mbar. 1 keV low energy Cs+with 10 nA current was used for the depth profiles acquired in this study to create a 140 mm by 140 mm area. The middle 50 mm by 50 mm area was analyzed using 0.3 pA Bi3 + primary ion beam. The standard HfO2 film used for quantification was doped with 1 � 1016ions per cm2Si4+and 5 � 1015ions per cm2Al3+. The depth of the crater generated by sputtering was measure with a Tencor P-20 long scan profiler. The depth resolution obtained using the experiment setting is between 2–3 nm. The negative secondary ion mass spectra were calibrated using H�, C�, O�, Hf�, HfO�and HfO2�. Experimental details of XRF can be found in a previous study.54,55   
 Lamella were prepared for STEM by focused ion beam, using an FEI Quanta to prepare the 27 nm-thick Gd-doped HfO2 (annealed at 650 1C for 20 s in N2 atmosphere) and using an FEI Helios nanolab 600i to prepare the 10 nm-thick Si-doped HfO2 thin film (annealed at 1000 1C for 1 s in N2 atmosphere). A probe-corrected FEI Titan G2 60–300 kV was operated at 200 kV

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trode materials, and the upper capping layer are reported to affect the polymorphism in doped HfO2 films.24However, the structural changes induced by the aforementioned factors are not clearly understood yet.

To date, perovskite-structure-based ferroelectrics have been the most intensively studied among the various ferroelectric

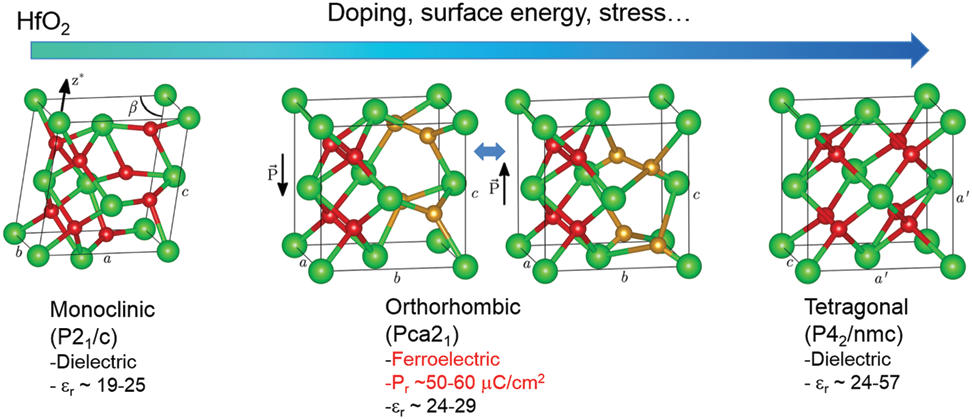


Fig. 1 The schematic diagram for the evolution of phases in doped HfO2 films and resulting electrical characteristics. The remanent polarization (Pr) and dielectric constant values (er) were taken from ref. 26. Reproduced with permission.26Copyright 2015, AIP Publishing LLC.

*J. Mater. Chem. C,* 2017, 5, 4677--4690 | 4679

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materials, and the structural origin of the spontaneous polariza-tion in perovskite materials is well understood based on the distortion of the oxygen octahedra.56The upper row of Fig. 2 compares the distortion of the oxygen octahedron in cubic and tetragonal perovskite structures. Generally, ABO3-type perovskites consist of two different cations (A and B) and oxygen ions (O). There are six oxygen ions (each oxygen ion is shared by two

Direct experimental observation of a small tilt of oxygen polyhedra is difficult even with state-of-the-art experimental tools and techniques. However, the aforementioned discussion is beneficial for understanding the structural evolution in fluorite ferroelectrics. In perovskite ferroelectrics, the tetragonality or c/a ratio is frequently used to simply describe the structural distortion.57–59The polar axis (c-axis) of the tetragonal perovskite

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| Published on 19 April 2017. Downloaded by Georgia Institute of Technology on 17/04/2018 06:05:05. | adjacent unit cells) in a unit cell, and they are located at the six | phase is generally larger by a few percent compared to the |
| face centers, while the B-site cation is located at the body center of | nonpolar axis (a-axis), so the tetragonality should be strongly |
| the unit cell. In the cubic phase, the charge centroids of the | related to the distortion of oxygen octahedron. The structural |
| cations and anions in a unit cell are equivalent due to the | evolution in a fluorite ferroelectric might be also qualitatively |
| existence of inversion symmetry, meaning that the phase cannot | similar to perovskite ferroelectrics. The crystal structure of the |
| be ferroelectric. When there is an elongation along the c-axis, | monoclinic phase is clearly different from the tetragonal or |
| however, the oxygen octahedron is distorted resulting in a for- | orthorhombic phase. However, distinguishing the orthorhombic |
| mation of the tetragonal phase. Therefore, the stable location of | from the tetragonal phase is very challenging especially given the |
| the B-site cation is displaced away from the center, and there are | fact that the Cu-Ka radiation used in standard lab equipment is |
| now two stable eccentric positions. This is the origin of the two | hardly sensitive to the oxygen in the presence of heavy atoms like |
| stable spontaneous polarization states in a tetragonal perovskite | Hf. It is reported that there is a large difference between the |
| material. An analogous discussion can be also derived for fluorite- | relative ratio of the longer axis to shorter axes of the orthorhombic |
| structure-based ferroelectrics, and the bottom row of Fig. 2 shows | and tetragonal phase.15,24Table 1 summarizes the lattice para- |
| the distortion of oxygen hexahedron (cubic coordination) in these | meters of both phases as reported in literature,15without con- |
| ferroelectrics (see also unit cells in Fig. 1). There are four metal | sidering lattice parameters obtained from polycrystalline thin |
| and eight oxygen ions in a unit cell of the fluorite structure. Metal | films, since the values might be a lattice parameters average of |
| ions are located at eight corners and six face centers, while oxygen | mixed phases. In summary, two important points should be |
| ions are located at the eight tetrahedral sites. One tetrahedron can | noticed. First, the aspect ratio (ra, specified as 2a/(b + c) for the |
| be constructed with one corner and three face centered metal | orthorhombic and c/a for the tetragonal phase) of the ortho- |
| ions. For the cubic phase, the oxygen hexahedron with body | rhombic phase is much larger than for the tetragonal phase. |
| centered metal ion can be found in two adjacent unit cells. When | The 2a/(b + c) of the orthorhombic phase was in the range of |
| there is an elongation along the a-axis of the cubic phase, the | 1.035–1.040,15while the c/a value of the tetragonal phase was in |
| ferroelectric orthorhombic phase can be formed. In this case, the | the range of 1.011–1.027.15This difference in ra was first pointed |
| location of four oxygen ions (whose coordination number is three, | out by Park et al. in 2013, and more recent results also showed a |
| yellow oxygen ions in Fig. 1) is significantly shifted (B13.8% of c | similar trend.15Accordingly, the change of the ra could serve as |
| lattice parameter26) from the stable position in a cubic phase, and | an indirect evidence for the phase evolution. Second, the differ- |
| each of them has two stable positions. There are also slight shifts | ence between b and c lattice parameters in the orthorhombic |
| in the position of the other four oxygen ions (red oxygen ions in | phase was smaller than 0.4%. Even from the structural analysis |
| Fig. 1 with four-fold coordination), but they amount to less than | on epitaxial Y-doped HfO2 films, the diffraction peaks from (020) |

1% of the c lattice parameter.

and (002) planes could not be distinguished from each other possibly due to the broadening of the diffraction peaks.44,46

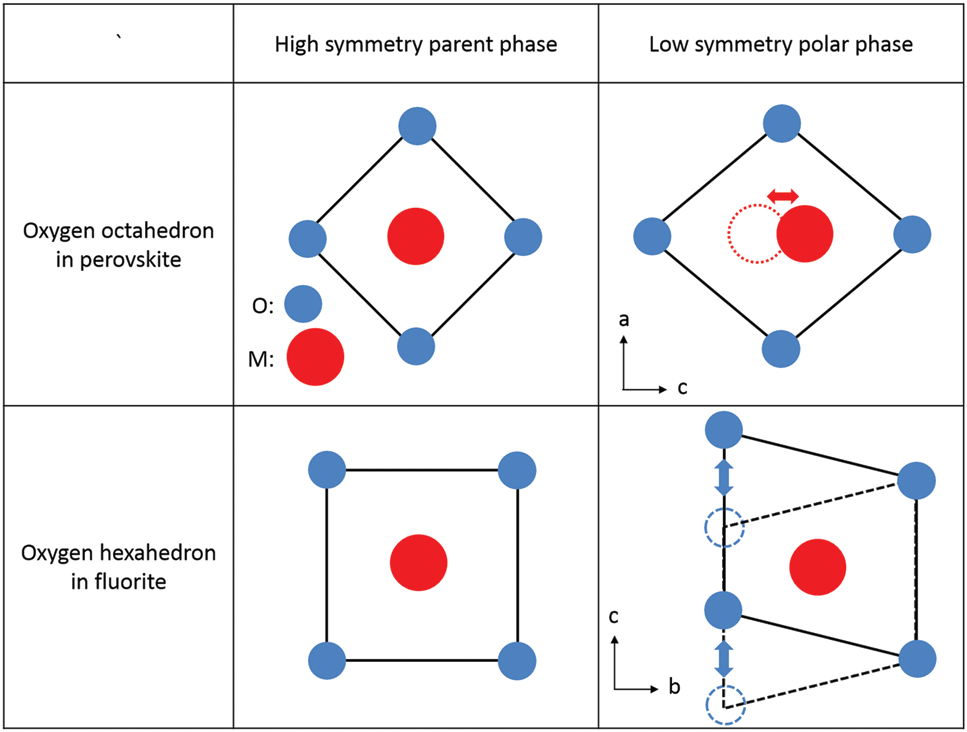


Fig. 2 A schematic for the structural origin of the ferroelectricity in perovskite and fluorite ferroelectrics.

4680 | *J. Mater. Chem. C,* 2017, 5, 4677--4690

Structural and chemical analysis based on STEM and secondary ionic mass spectrometry

To examine the structural and chemical properties of doped HfO2 films, Si-, Al-, and Gd-doped HfO2 films with various atomic layer deposition (ALD) cycle ratios (CR% = dopant/[dopant + Hf] � 100)

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| Table 1  sake of were tak | Lattice parameters of orthorhombic and tetragonal HfO2. For the  convenience, the lattice parameters from double sized unit cells  were taken for the tetragonal phase |

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Phase | a [Å] | b [Å] | c [Å] | ra | V [Å3] | Ref. |
| Orthorhombic | 5.10 | 4.90 | 4.92 | 1.041 | 123.19 | Zeng et al.66  Reyes-Lillo et al.67 Materlik et al.26 |
| Tetragonal | 5.07 | 4.88 | 4.89 | 1.038 | 120.99 |
| 5.23 | 5.04 | 5.06 | 1.036 | 133.38 |
| 5.06 | 5.20 | 1.027 | 133.29 | Zeng et al.66  Reyes-Lillo et al.67 Materlik et al.26 |
| 4.89 | 4.95 | 1.012 | 118.52 |
| 5.05 | 5.14 | 1.018 | 131.02 |

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were used. The detailed sample fabrication process and analysis techniques are included in the experimental procedure section. Measurements of correlation between ALD cycle ratio and the resulting dopant concentration by time of flight secondary ion mass spectrometry (TOF-SIMS) (for Si- and Al-doped HfO2 films), X-ray photoelectron spectroscopy (XPS) (for Si-60and Gd-doped

the O-[010]//M-[010] directions. The inset in Fig. 3a highlights the change in symmetry of the phases across the boundary (scale bar 1 nm). For Si-doped HfO2 films in Fig. 3b, on the other hand, an orthorhombic grain viewed down the [001] zone axis spans the thickness of the film, and relaxes towards tetragonal symmetry at the electrode interfaces. The existence of an inter-

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| Published on 19 April 2017. Downloaded by Georgia Institute of Technology on 17/04/2018 06:05:05. | HfO2 films7), time of flight elastic recoil detection analysis | | facial tetragonal phase was suggested to exist in doped HfO2 and |
| (TOF-ERDA) (for Al-doped HfO2 films), particle induced X-ray emission (PIXE) method (for Gd-doped HfO2 films61), and X-ray  fluorescence (XRF) are presented in Table 2. However, every | | HfO2–ZrO2 solid solution films,64and its transition to ferroelectric orthorhombic phase was described as one of the mechanisms behind the so-called wake-up effect.40From these STEM images, |
| method possesses unique issues for accurately estimating dopant | | the columnar grain structure are confirmed and the presence of |
| concentrations within doped HfO2 thin films, and the results | | different phases in HfO2 thin films are verified. |
| from different chemical analyses yield similar, though not equiva- | | Fig. 3c shows the depth profiles of ions of interest for |
| lent, results. Therefore, the ALD cycle ratio is used herein as the | | 10 nm-thick Si-doped HfO2 (ALD cycle ratio 1 : 26) film, which |
| described independent variable (instead of dopant concentration | | is the cycle ratio that achieves the highest Pr for Si-doped HfO2, |
| from the chemical analyses). The targeted doping concentrations | | using TOF-SIMS. Fig. 3d shows the secondary ion counts of |
| of Al- and Gd-doped HfO2 films in Table 2 were estimated from the growth rate of HfO2 and dopant oxide in previous studies.62,63 | | dopants as a function of depth in 10 nm-thick Si- (ALD cycle ratio 1 : 26), Al- (cycle ratio 1 : 32), and Gd-doped HfO2 (cycle |
| In those papers, the growth rate of HfO2 and dopant oxide was | | ratio 1 : 27) layers deposited on a TiN bottom electrode with or |
| systematically examined by controlling ALD cycle ratio and film | | without TiN top electrode, respectively. The depth was mea- |
| thickness. Ferroelectric doped HfO2 films are reported to have a | | sured using a profilometer after TOF-SIMS analysis. For Si- and |
| columnar grain structure with monoclinic, tetragonal, and ortho- | | Al-doped HfO2 thin films, modulations in the secondary ion |
| rhombic phase fractions. The crystalline structures of each grain | | counts from the dopants are clearly observed through the entire |
| can be distinguished using probe-corrected STEM (detailed techniques descriptions can be found in previous reports).25,40 | | depth of doped HfO2 thin films. In the case of the Si-doped HfO2, the distance between peaks in the Si�signal corresponds |
| From the STEM analysis of various regions of the films, mixed | | well to expected depths of high SiO2 concentration in the film |
| monoclinic, orthorhombic, and tetragonal phase regions are | | based on the chosen HfO2/SiO2 cycle ratio, which includes 4 |
| determined. In addition, the various orientations of each of these | | dopant layers for a 10 nm thick film. The 30 nm-thick Si-doped |
| phases are present in thin films. Fig. 3a and b show cross | | HfO2 film with the equivalent ALD cycle ratio was also exam- |
| sectional STEM images of 27 nm-thick Gd-doped and 10 nm | | ined by TOF-SIMS and a similar modulation of Si content could |
| Si-doped HfO2 layers between top and bottom TiN electrodes of a capacitor. In Fig. 3a, the Gd-doped HfO2 film shows a coherent | | be observed (data not shown). For the Al-doped HfO2 film, on the other hand, the AlO2� ion counts were constant in the bulk |
| interface between an orthorhombic grain and a monoclinic grain, where the O-[100] and M-[001] directions are oriented parallel to | | of the HfO2 grains, but higher at the interface between HfO2 and TiN electrodes, which may be caused by Al3+ion diffusion |
| each other along the viewing direction. The arrow indicates the | | to the interfacial regions. For the Gd-doped HfO2 film, the ion |
| boundary of the interface between the two phases, which is along | | counts of GdO�were relatively low compared to those of Si- and |
|  | Table 2 | The atomic layer deposition (ALD) cycle ratio and resulting doping concentrations for doped HfO2 films. ALD cycle ratio refers to relative cycle | |

ratio between Hf and dopant. (XPS: X-ray photoelectron spectroscopy, TOF-SIMS: time of flight secondary ion mass spectrometry, TOF-ERDA: time of

flight elastic recoil detection analysis, and PIXE: particle induced X-ray emission, XRF: X-ray fluorescence)

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Dopant |  | Sample#1 | Sample#2 | Sample#3 | Sample#4 | Sample#5 | Sample#6 | Sample#7 |
| Si | ALD cycle ratio [CR%] | 2.1 | 3.2 | 3.7 | 4.0 | 4.8 | 5.3 | 5.9 |
| Al | (Hf : Si)  XPS [%]50 | (46 : 1) | (30 : 1) | (26 : 1) | (24 : 1) | (20 : 1) | (18 : 1) | (14 : 1) |
| — | — | — | — | — | — | 5 |
| TOF-SIMS [%] | — | — | 2.0 | — | — | 2.8 | — |
| ALD cycle ratio [CR%] | 3.0 | 3.6 | 4.3 | 5.6 |
| Gd | (Hf : Al)  From growth rate [%]62 | (32 : 1) | (27 : 1) | (22 : 1) | (17 : 1) | 9.1 | 10.0 | 11.1 |
| 4.9 | 5.8 | 6.9 | 8.8 |
| TOF-SIMS [%] | 1.0 | — | — | 2.0 |
| TOF-ERDA [%] | — | — | — | 7.4 |
| ALD cycle ratio [CR%] | 3.6 | 4.2 | 5.0 | 6.7 |
| (Hf : Gd) | (27 : 1) | (23 : 1) | (19 : 1) | (14 : 1) | (10 : 1) | (9 : 1) | (8 : 1) |
| From growth rate/[%] GR/XPS [%]63  XPS [%]7  PIXE [%]61 | 3.5 | 4.2 | 5.0 | 6.7 | 9.1 | 10.0 | 11.1 |
| 2.0 | — | 3.0 | 7 | 9 | 6.0 | 11 |
| — | — |
| 3.4 | — |
| XRF [%] | 2.2 |

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|  | AlO2� in Si- and Al-doped HfO2 due to lower secondary ion yield |
| of GdO�. No sign of a modulation of GdO�ion counts could be |
| observed, but it does not necessarily mean that the Gd dopants |
| are distributed uniformly across the whole film. The modula- |
| tion strength might be influenced by the relatively low counts |
| and/or spatial inhomogeneity in the sputtering process of the |
| relatively thick TiN electrode. In addition, unlike the Si- and |
| Al-doped HfO2 samples, the TiN top and bottom electrodes in |
| the Gd-doped HfO2 sample were significantly oxidized. Strong  TiO2� and O2� counts are observed in both top and bottom TiN |
| electrodes via TOF-SIMS. However, this result does not mean |
| that TiN was oxidized into TiO2, and the existence of TiO2 |
| interfacial layer near Gd-doped HfO2 thin film could not be |
| detected by using STEM and GIXRD. Although an inhomoge- |
| neous distribution of dopants is observed for Si- and Al-doped |
| HfO2 films from TOF-SIMS, no sign of the formation of a |
| second phase could be observed in the highly doped regions |
| of the Si-doped samples from TEM. Further studies would be |
| required to examine the dopant impact on diffusion within the |
| dielectric, but this topic is not the main focus of this paper. |
| Structural analysis based on diffraction peaks in GIXRD |
| Several changes in GIXRD patterns with increasing ALD cycle ratio |
| and resulting dopant concentration have been reported.15,24,65–67 |
| J. Mu¨ller and Park independently reported the orthorhombic 221 |
| diffraction peak as a fingerprint of the ferroelectric orthorhombic |
| phase for Si-doped HfO2 and (Hf,Zr)O2 films, respectively, in their dissertations.68,69However, the intensity of this diffraction peak |
| was quite weak even with synchrotron X-ray radiation, and it |
| could not be employed to quantitatively extract the orthorhombic |
| phase fractions of the films. Another structural change observed |
| in literature was the shift of the 111 diffraction peak to higher 2y |
| region with increasing ALD cycle ratio in Si-doped HfO2 and (Hf,Zr)O2.15,24Although the shift of the diffraction peak is believed |
| to be strongly related to the phase evolution with increasing ALD |
| cycle ratio and resulting dopant concentration, this shift could not |
| be systematically and quantitatively examined. In this study, the |
| shifts of the o111 and o002 peaks are co-analyzed. Although the |
| o002 peak is in reality formed by overlap of the o020 and o002 |
| peaks, it will be called o002 for the sake of convenience. Here, xhkl |
| peak refers to the diffraction peak from hkl planes of the x phase, |
| and x can be m (monoclinic P21/c), o (orthorhombic Pca21), and t |
| (tetragonal P42/nmc). The changes in o111 and o002 peak location |
| can be seen in Fig. 4a and b, respectively. The shift of the o111 |
| peak towards higher 2y region with increasing ALD cycle ratio is |
| confirmed for all dopants, while the shift of o002 is rather weak. |
| This means that both the d111 distance (dhkl denotes the inter- |
| planar distance of the hkl planes) and the unit cell volume |
| decreases with increasing ALD cycle ratio. This phenomenon |
| could be related either to phase evolution or to generation of |
| internal stress effects dependent on the dopant size. It should be |

Fig. 3 High angle annular dark field scanning transmission electron micro-scopy (HAADF-STEM) images of (a) 27 nm-thick Gd-doped HfO2 (Gd:HfO2) and (b) 10 nm-thick Si-doped HfO2 (Si:HfO2) thin films, respectively. Time of flight secondary ion mass spectra of (c) 10 nm-thick Si-doped HfO2 for various secondary ions and (d) Si�, AlO2�, and GdO� counts for dopant ions in 10 nm-thick Si-, Al-, and Gd-doped HfO2 films, respectively.

4682 | *J. Mater. Chem. C,* 2017, 5, 4677--4690

noted that the radii of both Si4+and Al3+ions are smaller compared to an Hf4+ion, while the Gd3+ion is larger.65If the change in d111 and the unit cell volume relate to an internal stress effect derived from the dopant size within the Hf lattice, then both values should increase with increasing ALD cycle ratio for

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| Fig. 4 | 2y values for (a) o111/t101 and (b) o020/o002/t110 diffraction peaks as a function of cycle ratio. (c) The lattice parameters calculated from the | |
| peak locations and (d) their relative ratio (ra) as a function of cycle ratio. Cycle ratio (CR%) refers to ALD cycle number of dopants/(ALD cycle number of dopants + ALD cycle number of HfO2) � 100. | | |
| Published on 19 April 2017. Downloaded by Geo | Gd-doped HfO2 thin films. This is experimentally not the case. | | following assumptions: first, the diffraction peak at 35.4–35.9 |
| Therefore, the change of d111 and unit cell volume is expected to | | degrees is caused by a diffraction of o020/o002/t110 planes |
| relate to a phase change rather than an internal stress effect. | | without contribution from the o200/t002 planes. Second, b and |
| However, it is also noticed that the 2y value of the o111/t101 peak | | c lattice parameters of the orthorhombic phase are assumed to |
| for Gd-doped HfO2 films is generally lower than that of Si- and | | be equal to simplify analysis. In the introduction, it is discussed |
| Al-doped HfO2 films, meaning that the size of the dopant does | | that the difference within b and c lattice parameters was |
| also affect the d111 and the unit cell volume. | | smaller than 0.4% in a previous study,15and these two diffrac- |
| On the other hand, it should be mentioned that the strain | | tion peaks are indistinguishable even for the case of epitaxial |
| from (local) epitaxial relation between TiN bottom electrode | | films.26,44–46Fig. 4c shows the lattice parameters of doped HfO2 |
| and doped HfO2 thin films could be neglected. The interface | | films as a function of ALD cycle ratio. For Si-doped HfO2 films, |
| formed between TiN and doped HfO2 thin films is believed to | | the GIXRD patterns from samples with 2.1 and 3.2 CR% ALD |
| be disordered rather than epitaxial. The lattice parameter of | | cycle ratio were not considered in this analysis, since the films |

cubic TiN is about 0.424 nm,51while those of orthorhombic HfO2 is in the range of 0.509–0.535 nm.49Therefore, their differences are in the range of 20–26%, which are believed to be too large to expect an epitaxial relation between them. Schenk examined the texture of 30 nm-thick Si-doped HfO2 thin film and TiN electrode in his dissertation, and reported that the strongest texture is only three multiples of random distribution for both Si-doped HfO2 and TiN.44There might be an orientation relationship, but this relationship is not believed to be of a prototypical epitaxial type that gives rise to a certain strain in a specific crystallographic direction that can be easily argued to promote or inhibit the polar character of the poly-morphs of doped HfO2 thin films as in epitaxial films. There-fore, the epitaxial stress effect from TiN electrodes is not considered in this work.

From the locations of the o111 and o002 peaks, d111 and d002 can be calculated. In addition, the lattice parameters of the longest axis (a-axis for orthorhombic and c-axis for tetragonal phase) and shorter axes (b- and c-axis for orthorhombic and a-axis for tetragonal phase) could be determined using the

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predominantly crystallized in the monoclinic phase. The rela-tive fraction of the monoclinic phase will be determined later based on the Rietveld refinement results in the next section. Since the monoclinic phase possesses clearly distinguishable GIXRD patterns, quantitative analysis of its structure has been successfully conducted in literature.6In this study, the struc-tural changes observed during the phase transition from orthorhombic to tetragonal phase are intensively studied. The lattice parameters obtained for Gd-doped HfO2 thin films from GIXRD patterns were slightly smaller than those for the ortho-rhombic phase measured using STEM in a previous study.25 However, it should be noted that the lattice parameters taken from GIXRD patterns are averages of lattice parameters of orthorhombic and tetragonal phases, whereas the lattice para-meters of specific crystalline phase in nanoscale grains can be measured using STEM.25As expected from Fig. 4b, the shorter axis of Gd:HfO2 films are generally larger than those of Si- and Al-doped HfO2 films, and the length of the shorter axis is generally found to increase with dopant size. With variations in ALD cycle ratio, the changes in the two shorter lattice

*J. Mater. Chem. C,* 2017, 5, 4677--4690 | 4683

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parameters are negligible for all the dopants. The changes in the longest lattice parameters are much stronger than that of the two shorter axes lattice parameters. With increasing ALD cycle ratio, the longest lattice parameter decreases for all dopants. From these lattice parameters, ra is calculated and plotted versus the dopant content (Fig. 4d). The largest ra value

parameters of the crystalline phases of HfO2. The effect of dopants will be discussed in more detail later in the next

Section 5. For Si-doped HfO2 thin films with CR% lower than 4.8, the Rwp values are within 20–26%. From the fitted diffraction patterns and resulting Rwp values, it could be concluded that the diffraction patterns were fitted with errors within reasonable

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| Published on 19 April 2017. Downloaded by Georgia Institute of Technology on 17/04/2018 06:05:05. | of 1.033 is observed for the smallest ALD cycle ratio for | range via Rietveld refinement. The Rwp values seem rather higher compared to the typical values (o10%) in Rietveld refinements |
| Al-doped HfO2 films (3 CR%). However, the value decreases to |
| 0.989 with increasing ALD cycle ratio to 5.6 CR%. The largest ra | of single crystals or polycrystalline ceramics.72However, for the |
| values for Si- and Gd-doped HfO2 films were 1.014 and 1.010, | case of doped thin polycrystalline films in this study, numerous |
| respectively, and they decreased to 0.991 and 0.984 with | factors including film stress, doping, and preferred orientation, |
| increasing ALD cycle ratio to 4.8 and 10 CR%, respectively. This | can make an ideal fit impossible, thus increasing the Rwp values.72 |
| decrease in ra values is believed to be strongly related to the | It should be noted that the Rwp values in this study is quantita- |
| phase evolution in the HfO2 based films. According to previous | tively similar with those in previous Rietveld refinement results |
| reports, doped HfO2 films are polycrystalline with columnar | conducted on thin or thick films73–76and some powders.77–81 |
| grains, and multiple phases such as monoclinic, tetragonal, | Fig. 6a–c show the changes in the relative fraction of the |
| and monoclinic are simultaneously present in the layers.24,25 | monoclinic (rmono), tetragonal (rtetra), and orthorhombic (rortho) |
| Although the change in ra values qualitatively shows that there | phase as a function of cycle ration in Si-, Al-, and Gd-doped |
| might be phase change from orthorhombic to tetragonal phase | HfO2 films, respectively. For the case of pure HfO2 and 2.1–3.2 CR% |
| occurring with respect to CR%, the phase evolution cannot be | Si doped HfO2 films, more than 85% of the films are of monoclinic phase, which is in good agreement with previous results.24,65 |
| quantitatively analyzed solely based on the shift of diffraction |
| peaks. Therefore, a Rietveld refinement70was conducted to | However, the fraction of the monoclinic phase is less than 20% |
| quantitatively examine the phase evolution in doped HfO2 films. | when the ALD cycle ratio is higher than 3.7, 3.0, and 3.6 CR% for |
| Results of Rietveld refinement and comparison to the | Si-, Al-, and Gd-doped HfO2 films, respectively. Above these ALD |
| cycle ratios, the ferroelectric orthorhombic phase is the most |
| ferroelectric properties |
| prominent phase in doped HfO2 films. The changes in the relative |
| Fig. 5a–c show the GIXRD patterns and fitted curves using | phase fraction of the orthorhombic phase and pristine Pr values |
| Rietveld refinement of 3.7 CR% Si-, 3.0 CR% Al-, and 3.6 CR% | with variation in ALD cycle ratio will be discussed in Fig. 7 and the |
| Gd-doped HfO2 thin films. Bottom panels of Fig. 5a–c show the | corresponding text in greater detail. For the case of Si-doped HfO2 |
| diffraction patterns of monoclinic, tetragonal, and orthorhombic | films, the ALD cycle ratio range where the relative fraction of |
| phase. The details of Rietveld refinement using TOPAS software are | orthorhombic phase is higher than 20% is very narrow. Only |
| included in the experimental section. The weighted profile R-factor | 3.7 and 4.0 CR% Si-doped films showed an rortho value larger than |
| (Rwp), which shows the quality of refinement quantitatively,71,72lies | 50%, and the rortho value abruptly decreased to 2.7% when ALD |
| within 20–31, 20–26, and 17–21.5% for Si-, Al-, and Gd-doped HfO2 | cycle ratio increased to 4.8 CR%. For the case of Al-doped HfO2 |
| thin films, respectively. Rwp values were the largest (26–31%) for | films, the largest fraction of orthorhombic phase (B77%) is |
| Si-doped HfO2 films with CR% higher than 4.8, which might be | observed for an ALD cycle ratio of 3 CR%, and it is still about |
| related to the effect of dopant size and concentration on lattice | 66% for an ALD cycle ratio of 3.6 CR%. However, with an increasing |

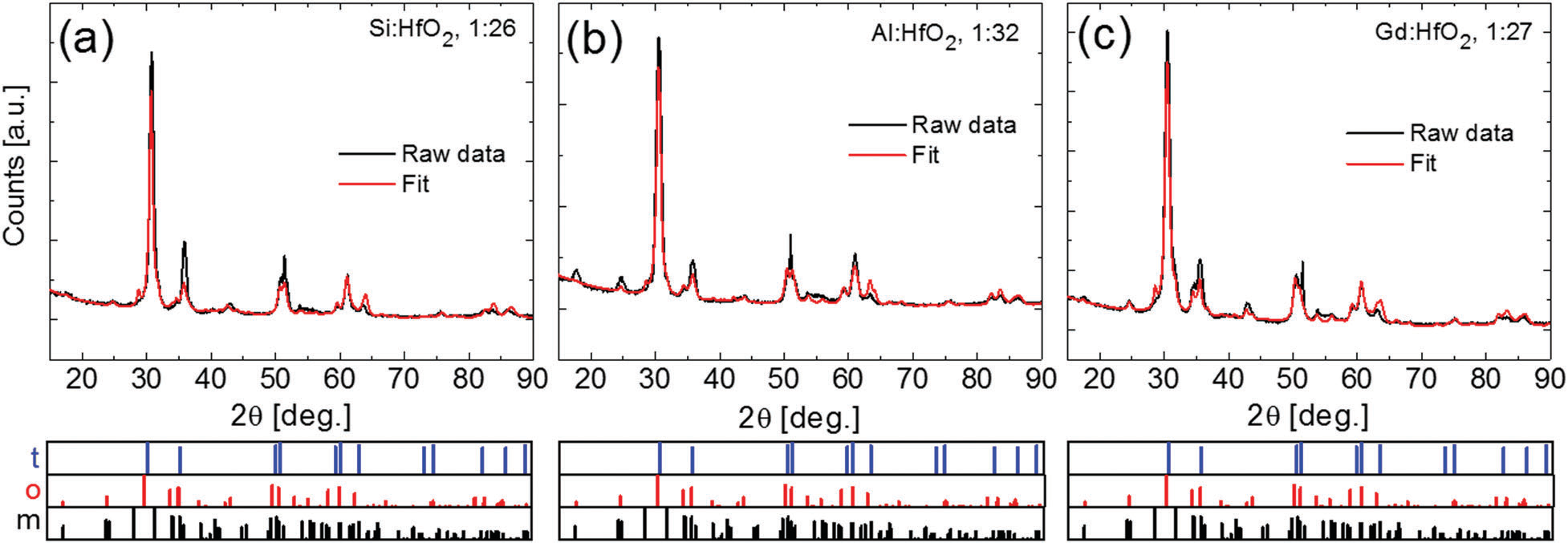


Fig. 5 GIXRD patterns with Rietveld refinement results for (a) Si- (3.7 CR%), (b) Al- (3.0 CR%), and (c) Gd- (3.6 CR%) doped HfO2 thin films. Bottom panels

show diffraction patterns for tetragonal (t), orthorhombic (o), and monoclinic (m) phases from crystallographic information files. The intensities of

diffraction peaks in reference patterns in bottom panels are plotted in log scale (from 1 to 100%) to clearly show the locations of weak diffraction peaks.

4684 | *J. Mater. Chem. C,* 2017, 5, 4677--4690

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| Fig. 6 | | Relative fraction of monoclinic, tetragonal, and orthorhombic phase in (a) Si-, (b) Al-, and (c) Gd-doped HfO2 films as a function of cycle ratio. | |
| (d) Comparison of the relative portion of the orthorhombic phase taken from (a)–(c). The calculated errors in phase fractions are added as error bars. Cycle ratio (CR%) refers to ALD cycle number of dopants/(ALD cycle number of dopants + ALD cycle number of HfO2) � 100. | | | |
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| Fig. 7 | (a) Pristine Pr before wake-up and field cycling as a function of cycle ratio. (b) Pristine Pr versus orthorhombic phase portion. The red dashed line | | |

shows the linear fit. Cycle ratio (CR%) refers to ALD cycle number of dopants/(ALD cycle number of dopants + ALD cycle number of HfO2) � 100.

ALD cycle ratio beyond 4.3 CR%, the rortho value decreases to about 23%. For the case of Gd-doped HfO2 films, rortho is higher than

cycle ratio range is universal for all potential dopants. In fact, the cycle ratio of 50% and 2.6% were reported for Zr6and Sr8doping

57% within the ALD cycle ratio range of 3.6–4.2 CR%, and the in previous studies.

largest fraction is about 73% for a 4.2 CR% ALD cycle ratio. However, rortho decreased to 38 and 16% when the ALD cycle ratio increases to 6.7 and 10.0 CR%, respectively. The changes in rortho are summarized for doped HfO2 films in Fig. 6d. As seen in the Fig. 6d, the CR% for the largest orthorhombic phase fraction is in the range of 3–4.2%, and similar for all the three dopants used in this study. Even though the exact dopant content could not be clearly determined by the characterization methods used in Table 2, we would conclude that the maximum ferroelectric properties are reached in a dopant range of about 2–3 mol% for all three dopants. However, it does not necessarily mean that this

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As mentioned before, the ALD cycle ratio range for a high orthorhombic phase fraction is narrower for Si-doped HfO2 in comparison to Al- and Gd-doped HfO2 films. In fact, the monoclinic to orthorhombic phase transition is difficult to analyze since even small dopant amounts already reduce the monoclinic phase fraction drastically. Here, one ALD cycle of dopant oxide every 30–40 HfO2 cycles has a strong impact. However, the phase evolution from the orthorhombic to tetra-gonal phase is the most abrupt in the Si-doped HfO2 films among the three dopants used in this study. This trend is consistent with the trend in pristine Pr values shown in Fig. 7a.

*J. Mater. Chem. C,* 2017, 5, 4677--4690 | 4685

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| It should be noted that the pristine Pr values in this study are |  | |
| rather low compared to those in literature, since the Pr value is taken before the common wake-up field cycling.64,82–89The Pr |
| values of doped HfO2 films have been reported to strongly relate to phase evolution during electric field cycling.84–90For |
| the case of Si-doped HfO2 films, a pristine Pr value larger than |
| 5 mC cm�2is observed only for 3.7 and 4.0 CR% ALD cycle ratios. |
| For the case of Al- and Gd-doped HfO2 films, on the other hand, a Pr value larger than 5 mC cm�2is detected within an ALD cycle |
| ratio range of 3.0–3.6 and 3.6–5.0 CR%, respectively. Although |
| the ALD cycle ratio ranges for Pr larger than 5 mC cm�2seem |
| similar for Si- and Al-doped HfO2 films, the actual dopant |
| concentration range in Al-doped HfO2 film for Pr larger than 5 mC cm�2might be much wider when a higher growth rate of |
| TMA is considered.62,63(see targeted doping concentrations in |
| Table 2.) The largest pristine Pr value observed amongst all | Fig. 8 | Unit cell volume as a function of ionic radius of dopants. The ionic |
| radii were taken from ref. 88 and 89. For the case of Si and Al, the ionic radii | |
| dopants and films here is that of the 3.0 CR% ALD cycle ratio Al- |
| doped HfO2 film, which also possesses the largest ra value in | for eight fold coordination were calculated from extrapolation. | |
| Published on 19 April 2017. Downloaded by Georgia Institute of | Fig. 4d. From Fig. 6a and d, a strong relationship between rortho | with Si doping compared to the Al and Gd doping case. This | |
| and pristine Pr is expected, which can be confirmed in Fig. 7b. |
| From a linear fitting, the expected Pr value of 100% ortho- |
| rhombic fraction was B15.4 mC cm�2, which was smaller than | can be understood based on the change in metal–oxygen bond | |
| the theoretical value (B35 mC cm�2) expected for randomly | length. Lee et al. examined the change of free energy for the | |
| oriented orthorhombic HfO2 films.53However, it should be | monoclinic, tetragonal and cubic phases in HfO2 doped with various dopants using first principle calculations.96In their | |
| noted that the pristine Pr can also be affected by other factors |
| such as film texture,90dead layer thickness,91film thickness,92 | report, the relative free energy of the tetragonal phase com- | |
| grain size,93degree of crystallinity,94and the distribution of | pared to the stable monoclinic phase could be reduced by | |
| defects including oxygen vacancies.95Despite these various | doping with ions smaller than Hf.96Especially of note, Si | |
| factors, however, a strong linear relation implies that the | doping could decrease the relative free energy of the tetragonal | |
| ferroelectricity in doped HfO2 films is fundamentally governed | phase significantly compared to that of the monoclinic phase.96 | |
| by the polymorphism of the films. | The relative free energy of the cubic phase also decreased with | |
| Comparison between dopants | Si doping, but the magnitude of the decrease was much smaller | |
| than for the tetragonal phase.96A similar but weaker trend | |
| Based on rortho and pristine Pr data, the change from ortho- | could be observed for Al doping.96For Gd doping on the other | |
| rhombic to tetragonal phase occurs most abruptly for Si-doped | hand, the decrease of the free energy of the cubic phase was | |
| HfO2 films. This means that the Si dopant effectively acceler- | larger than for the tetragonal phase.96The different behavior | |

ates the phase change from the orthorhombic to tetragonal phase and could be related to the relatively large decrease in unit cell volume due to the small ionic radius of Si. Fig. 8 shows the unit cell volume of the orthorhombic and tetragonal phase in doped HfO2 films. The unit cell volume of the orthorhombic phase was calculated for films with the largest Pr value, whereas that of the tetragonal phase was taken from an ALD cycle ratio with Pr values below 3 mC cm�2. For both orthorhombic and tetragonal phases, the unit cell volume decreases with smaller dopant size. The trend of decreasing cell volume for smaller dopants is in good agreement with STEM measurements, though the volumes obtained by GIXRD are slightly smaller than those measured via STEM (134.4 Å3for Gd-doped HfO2 based on volume = abc using a = 5.24, b = 5.06, and c = 5.07,25 and 132.1 Å3for Si-doped HfO2 based on volume = ab2using a = 5.22 Å and b = 5.03 Å as measured from the center of the grain in Fig. 3b). For all dopants, the unit cell volume of the tetragonal phase is smaller than for the orthorhombic phase, which is well-matched with previous studies.26,66,67Therefore, the free energy of the tetragonal phase might further decrease

4686 | *J. Mater. Chem. C,* 2017, 5, 4677--4690

for the examined dopants could be understood based on changes in the metal–oxygen bond length.96Table 3 shows the metal–oxygen bond length of tetragonal and orthorhombic HfO2, which were calculated based on computational results.26 For the case of the tetragonal phase, two different metal oxygen bond lengths of 2.08 and 2.34 Å are determined. When an Si4+ ion replaces one Hf4+ion, the Si–O bond length can decrease to 1.69 Å, which is very similar with the ideal Si–O bond length (1.63 Å) in a quartz SiO2 structure.96Moreover, the O–Si–O angle values (105.41 or 117.91) are also very similar to that in the quartz lattice (108.91–110.51).96As a result, the relative free energy of the tetragonal phase can decrease significantly com-pared to the monoclinic or cubic phases.96As seen in Table 3, the bond lengths of the orthorhombic phase are very different from the tetragonal phase, and the coordination numbers of oxygen ions are also different: all fourfold in tetragonal and half fourfold and half threefold in the orthorhombic phase.26In fact, the coordination number of oxygen ions in the ortho-rhombic is similar compared to those in the monoclinic phase. Although the lattice parameters of the orthorhombic phase are

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Table 3 Hf–O bond length in orthorhombic and tetragonal HfO2. The Moreover, partial oxidation of the TiN bottom electrode was

bond length was calculated from the lattice parameters and relative ionic locations in ref. 26. O3 and O4 refer to threefold and fourfold bounded oxygen, respectively

reported for TiN/Hf0.5Zr0.5O2/TiN capacitor structures.102Overall, the Si diffusion seems much weaker in HfO2 thin films com-pared to the Al and Gd diffusion. Differences in the diffusivity of

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Phase | Oxygen type | I [Å] | II [Å] | III [Å] | IV [Å] | Si4+and Al3+/Gd3+might be attributed to a different valence |

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Orthorhombic | O3 | 2.243 | 2.721 | 2.773 | — |
| O4 | 2.231 | 2.238 | 2.324 | 2.334 |

number of the dopants and resulting different oxygen vacancy concentration.103Si4+is a tetravalent ion, while Al3+and Gd3+are

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| 05. | Tetragonal | O4 | 2.078 | 2.078 | 2.336 | 2.336 | trivalent. Therefore, one oxygen vacancy might be included into |
| the HfO2 lattice for every two Al3+or Gd3+dopant ions, and the |
| Published on 19 April 2017. Downloaded by Georgia Institute of Technology on 17/04/2018 06:05: | very similar to those of the tetragonal phase, the coordination | | | | | |  |
| oxygen vacancies might facilitate the diffusion of dopants by |
| lowering the kinetic barrier.103Due to the relatively low diffusivity |
| numbers of Hf4+and O2�ions in the orthorhombic phase are | | | | | | of Si, some heavily doped regions might be formed in Si-doped |
| similar to those in the monoclinic phase. In the orthorhombic | | | | | | HfO2, and they might be detrimental for the formation of the |
| phase, the metal–oxygen bond lengths of threefold oxygen ions | | | | | | ferroelectric orthorhombic phase. However, further studies are |
| are 2.24, 2.72, and 2.72 Å, while the metal–oxygen bond lengths | | | | | | needed to examine the effect of diffusivity. Varying oxygen vacancy |
| of fourfold oxygen ions are 2.23, 2.24, 2.32, and 2.33 Å. | | | | | | levels for trivalent dopants are also considered as one potential |
| Different from the tetragonal phase, the smallest bond length | | | | | | cause for the effect of dopants on the ALD cycle ratio range for |
| of orthorhombic phase is 2.23 Å with no short metal–oxygen | | | | | | ferroelectric phase formation. However, the narrowest ALD cycle |
| bonds. The shortest bond length is even larger than for the | | | | | | ratio range in Si-doped HfO2 cannot be understood by the direct |
| cubic phase (B2.18 Å), and it might not be decreased more | | | | | | effect of oxygen vacancies. Oxygen vacancies are reported to |
| significantly than for Si:HfO2 in the tetragonal phase. There- | | | | | | further stabilize the tetragonal phase compared to the orthor- |
| fore, the ALD cycle ratio region for ferroelectric properties in Si | | | | | | hombic phase.61Therefore, the additional oxygen vacancy doping |
| doped HfO2 films might be quite narrow. A similar effect is | | | | | | with Al and Gd doping is expected to decrease the ALD cycle ratio |
| expected for Al-doped HfO2, with an ideal Al–O bond length in | | | | | | range for ferroelectric orthorhombic phase, which is the opposite |
| corundum Al2O3 (1.92 Å) being about 14% smaller compared to | | | | | | from what is experimentally observed. |
| the Hf–O bond length in cubic HfO2. Therefore, the ALD cycle | | | | | | Conclusions |
| ratio range for ferroelectric properties with Al doping might be | | | | | |
| larger than for Si doping. For the case of Gd3+, the ideal Gd–O | | | | | |
| bond length should be even larger than for Al–O due to the | | | | | |
| larger ionic radius of Gd3+(105 pm) in relation to Al3+(69 pm) | | | | | | In conclusion, the structural changes within HfO2 thin films |
| and Si4+(54 pm).97,98The ionic radii were taken from a previous | | | | | | doped with Si, Al, and Gd were systematically examined. |
| study by Shannon for eight fold coordination condition.97For | | | | | | To quantitatively investigate changes in the GIXRD patterns, |
| the cases of Al and Si, there was no ionic radius data within | | | | | | Rietveld refinement was conducted on these films for the first |
| eight fold coordination, so the values were estimated by extra- | | | | | | time. Here, a strong linear relationship between the ortho- |
| polating the ionic radii in four to six fold coordination.98As a | | | | | | rhombic phase fraction and the pristine remanent polarization |
| result, the orthorhombic phase can be formed within an even | | | | | | value confirms the original hypothesis, demonstrating that the |

larger ALD cycle ratio range compared to Al-doped HfO2 films.

Other possible causes for a dopant dependence of ALD cycle ratio range for strong ferroelectric properties were also exam-ined. The difference in the spatial distribution of dopants might be another possible reason. From TOF-SIMS results in Fig. 3d, the diffusion of Si seems weaker compared to those of Al and Gd. For the case of Al-doped HfO2 films, the homogeneous distribution of Al was reported in some previous studies from TOF-SIMS results and Auger electron spectroscopy.99,100The diffusion of Al toward interfacial region could not be observed in these studies.99,100The ALD and annealing process in the studies from ref. 99 and 100 was very similar to those in this study, but different results were observed possibly attributed to a different electrode. In those papers, a Si or Mo electrode was applied while a TiN electrode was used in our study.99,100The TiN electrode is expected to partially scavenge oxygen atoms from the HfO2 in interfacial regions introducing a higher oxygen vacancy concentration, which might affect diffusion of Al dopants. It is well known that the TiN top electrode can reduce the interfacial SiO2 layer between HfO2 and the Si substrate.101

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underlying ferroelectric response is strongly coupled to the orthorhombic phase fraction of the fluorite crystal structure. The methodology used in this study provides a framework for studying the newly reported nanoscale fluorite ferroelectrics. Although the HfO2 thin films doped with Si, Al, and Gd were studied here, this structural analysis is believed to be widely applicable even to the fluorite ferroelectrics with different matrix and dopant materials.

The largest Pr and orthorhombic phase fraction can be observed within the cycle ratio range of 3–4.2 CR%, which is believed to be the doping concentration range of 1–3 cat% for all three dopants. The ALD cycle ratio region for ferroelectric properties was the narrowest for Si-doped HfO2, and increased with increasing dopant size. This can be qualitatively under-stood based on a metal–oxygen bond length model. The shorter Hf–O bond length in the tetragonal phase is much smaller than in the orthorhombic phase. Therefore, Si doping might decrease the relative free energy of tetragonal phase more significantly compared to the orthorhombic phase. This effect may become weaker with increasing dopant size.

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**[View Article Online](http://dx.doi.org/10.1039/C7TC01200D)** Paper Journal of Materials Chemistry C

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