

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Published on 14 June 2017. Downloaded by Georgia Institute of Technology on 11/11/2017 03:33:50. | Nanoscale |  | | | | | | | |
| PAPER | **[View Article Online](http://dx.doi.org/10.1039/C7NR02121F)** | | | | | | | |
| **[View Journal](http://pubs.rsc.org/en/journals/journal/NR)  [| View Issue](http://pubs.rsc.org/en/journals/journal/NR?issueid=NR009028)** | | | | | | | |
|  | Surface and grain boundary energy as the | | | | | | | |
| key enabler of ferroelectricity in nanoscale | | | | | | | |
| Cite this: Nanoscale, 2017, 9, 9973 |
| hafnia-zirconia: a comparison of model and | | | | | | | |
| Received 25th March 2017, | experiment† | | | | | | | |
| Min Hyuk Park, |  | a,b Young Hwan Lee,a Han Joon Kim,a Tony Schenk, | | |  | b | |
| Woongkyu Lee,aKeum Do Kim,aFranz P. G. Fengler,aThomas Mikolajick, | | | | | |  | b,c |
| Uwe Schroeder |  | \*band Cheol Seong Hwang |  | \*a | | | |
| The unexpected ferroelectric properties of nanoscale hafnia-zirconia are considered to be promising for | | | | | | | |
| a wealth of applications including ferroelectric memory, field effect transistors, and energy-related appli- | | | | | | | |
| cations. However, the reason why the unexpected ferroelectric Pca21 phase can be stabilized has not | | | | | | | |
| been clearly understood although numerous extensive theoretical and experimental results have been | | | | | | | |
| reported recently. The ferroelectric orthorhombic phase is not a stable phase under processing con- | | | | | | | |
| ditions from the viewpoint of bulk free energy. Although the possibility of stabilization of the ferroelectric | | | | | | | |
| phase due to the surface energy effect has been theoretically suggested, such a theoretical model has | | | | | | | |
| not been systematically compared with actual experimental results. In this study, the experimental obser- | | | | | | | |
| vations on polymorphism in nanoscale HfO2–ZrO2 solid solution thin films of a wide range of film com- | | | | | | | |
| positions and thicknesses are comprehensively related to the theoretical predictions based on a thermo- | | | | | | | |
| dynamic surface energy model. The theoretical model can semi-quantitatively explain the experimental | | | | | | | |
| results on the phase-evolution, but there were non-negligible discrepancies between the two results. To | | | | | | | |
| understand these discrepancies, various factors such as the film stress, the role of a TiN capping layer, and | | | | | | | |
| the kinetics of crystallization are systematically studied. This work also reports on the evolution of electri- | | | | | | | |
| Accepted 12th June 2017 | cal properties of the film, i.e. dielectric, ferroelectric, anti-ferroelectric, and morphotropic phase changes, | | | | | | | |
| DOI: 10.1039/c7nr02121f | as a function of the film composition and thickness. The in-depth analyses of the phase change are | | | | | | | |
| rsc.li/nanoscale | expected to provide an important guideline for subsequent studies. | | | | | | | |

Introduction

The properties of nanoscale materials are different from those of bulk materials in many cases.1–4This difference generally results from the different crystallographic phases in nanoscale materials from those in bulk materials, and it is generally related to the large surface to volume ratio.1–4The total free energy of a certain material is the sum of the bulk free energy and the surface (or the interface and grain boundary for

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| heterogeneous | and | polycrystalline | materials) | energy.1–4 |

aDepartment of Materials Science & Engineering and Inter-university Semiconductor Research Center, Seoul National University, Seoul 151-744, Korea.

E-mail: cheolsh@snu.ac.kr   
bNaMLab gGmbH, Noethnitzer Strasse 64, 01187 Dresden, Germany.

E-mail: Uwe.Schroeder@namlab.com   
cChair of Nanoelectronic Materials, TU Dresden, 01062 Dresden, Germany  
†Electronic supplementary information (ESI) available. See DOI: 10.1039/ c7nr02121f

This journal is © The Royal Society of Chemistry 2017

Therefore, with a significant grain size decrease, metastable phases with a low surface energy can be stabilized.1–4In 2011, feasible ferroelectric properties were first reported from doped HfO2,5which is supposed to be a high-k dielectric layer. Although the origin of such an unexpected emergence of ferroelectric properties was not clearly elucidated in the orig-inal report,5it is believed that a new polar orthorhombic phase (o-phase, space group: Pca21, no. 29) is involved,6,7and many similar reports have been published on the pure8or doped-HfO2 9–18 (or unintentionally doped HfO2 19), Hf1−xZrxO2 (HZO, x = 0.0–1.0),20–24and even ZrO2 25,26 films.27 In fact, this polar phase was first reported in Mg-doped ZrO2 films in 1998, but its ferroelectricity was not examined at that time.28The polymorphs of HfO2 and ZrO2 were systematically examined by Navrotsky and Pitcher et al. based on thermodynamic free energy.29,30It has been reported that the new ferroelectric phase can be utilized for 1T-1C ferroelectric random-access-

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| memory | (FeRAM), | | 1T | ferroelectric | field | effect | transistor |
| (FeFET) | and | negative | | capacitance | field-effect-transistor | | |

Nanoscale, 2017, 9, 9973–9986 | 9973

**[View Article Online](http://dx.doi.org/10.1039/C7NR02121F)** Paper Nanoscale

(NCFET) applications.31–33Moreover, the phase transition involved in the ferroelectric o-phase has been reported to be promising for energy storage, energy harvesting, and electro-caloric cooling.34–39The stable phase of the bulk HfO2 and ZrO2 is the monoclinic phase (m-phase, space group: P21/c, no. 14), and no polar phase can be observed in the phase diagram of

Materlik et al.’s paper.42The actual grain size distribution was extracted from plane-view scanning electron microscopy (SEM) images using the computational software Gwyddion.51The cal-culated grain size distribution was used to calculate the expected relative fractions of the t-, o-, and m-phases in the film. The verification of the crystalline phases in ferroelectric

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Technology on 11/11/2017 03:33:50. | the bulk HfO2 and ZrO2.40,41On increasing the temperature, | | | | | | doped | HfO2 | | films | was | done | by | transmission | | | electron | |
| tetragonal (t-phase, space group: P42/nmc, no. 137) and cubic | | | | | | microscopy (TEM) studies,6,7but the well-known difficulty in | | | | | | | | | | | |
| phases (c-phase, space group: Fm3ˉm, no. 225) can be stabil- | | | | | | discerning the diffraction peaks from the three phases in | | | | | | | | | | | |
| ized, while two nonpolar orthorhombic phases (space groups: | | | | | | general | X-ray | | analysis | | renders | | quantitative | | verification | | |
| Pbca, no. 61 and Pnma, no. 62) can be formed with increasing | | | | | | difficult.6,21Therefore, experimental phase identification is | | | | | | | | | | | |
| hydrostatic compressive pressure for both HfO2 and ZrO2.40,41 | | | | | | mostly based on the assessment of the dielectric properties, | | | | | | | | | | | |
| Therefore, the emergence of the unexpected polar phase must | | | | | | e.g. the measurement of the polarization hysteresis. Especially, | | | | | | | | | | | |
| be attributed to other factors than the bulk properties. In | | | | | | the differences between the theoretically expected polymorph- | | | | | | | | | | | |
| 2015, Materlik et al. first suggested that the o-phase can be | | | | | | ism and the experimentally observed electrical properties | | | | | | | | | | | |
| stabilized due to the surface energy effect based on their com- | | | | | | are systematically compared, and the possible origins of such | | | | | | | | | | | |
| prehensive first principles calculations.42According to their | | | | | | differences are carefully discussed. | | | | | | | | | | | |
| report, the surface energy of the t-phase was much lower than | | | | | |
| of | that of the m-phase, whereas the bulk free energy of the | | | | | | Experimental | | | | | | | | | | | |
| tute | |  | | --- | | t-phase was higher than that of the m-phase, which is consist- | | | | | | |
| Published on 14 June 2017. Downloaded by Georgia Insti | ent with the experimental results for bulk-phase materials.42 | | | | | |
| Sample preparation | | | | | | | | | | | |
| The bulk and the surface free energies of the o-phase were in | | | | | |
| between those of the t- and m-phases.42As a result, within | | | | | | HZO films were deposited on a Si substrate coated with a TiN | | | | | | | | | | | |
| certain thickness and grain size ranges, thermodynamic stabi- | | | | | | electrode using thermal ALD at a wafer temperature of 280 °C. | | | | | | | | | | | |
| lization of the o-phase could be understood based on the | | | | | | Hf[N(C2H5)CH3]4, Zr[N(C2H5)CH3]4, and ozone were used as | | | | | | | | | | | |
| surface (or grain boundary) energy model.42The theory for the | | | | | | the Hf precursor, Zr precursor, and oxygen source, respectively. | | | | | | | | | | | |
| stabilization of the t-phase in ZrO2 thin films or nanoscale | | | | | | 50 nm-thick TiN films were deposited onto the thermally oxi- | | | | | | | | | | | |
| crystallite due to the surface energy effect has already been | | | | | | dized Si substrate and used as the bottom electrode. HZO | | | | | | | | | | | |
| known to explain the experimental observations within thin | | | | | | films with various Hf/(Hf + Zr) ratios were prepared by control- | | | | | | | | | | | |
| films and nanoscale crystallites.43–46The surface energy was | | | | | | ling the ALD cycle ratios of HfO2 and ZrO2, with almost identi- | | | | | | | | | | | |
| calculated using computational methods and has been useful | | | | | | cal growth rates of HfO2 and ZrO2 (∼0.12 nm per cycle on the | | | | | | | | | | | |
| in | predicting | and | explaining | relatively | unusual | TiN electrode). For scanning electron microscopy (SEM) ana- | | | | | | | | | | | |
| experiments.47–49However, the surface energy of the o-phase | | | | | | lysis, the HZO films were annealed without the TiN capping | | | | | | | | | | | |
| had not been considered before Materlik et al.’s work.42Due to | | | | | | electrode (post-deposition-annealing: PDA). However, it was | | | | | | | | | | | |
| the availability of critical information on the o-phase, it is now | | | | | | confirmed that the presence of TiN capping layers during | | | | | | | | | | | |
| feasible to compare the experimentally acquired results to the | | | | | | annealing | | did | not | significantly | | | alter | the | grain | | size |
| theoretically predicted phase evolution behaviours of HZO- | | | | | | distribution. | | | | | | | | | | | |

based ferroelectric films. However, possible discrepancies between the actual experimental results and the surface energy model should still be quantitatively examined. Since the precise grain size distribution from the experiment was not available for Materlik et al.’s theoretical calculations,42the grain size was assumed to be a fixed value. However, because almost all polycrystalline materials have a certain grain size distribution, which must have a crucial impact on the phase evolution, such effects need to be considered.

Electrical and physical characterization

For electrical characterization, Pt (60 nm)/TiN (20 nm) top electrodes were deposited using a shadow mask and RF mag-netron sputtering. After the top electrode deposition, post metallization annealing (PMA) was performed at 500 °C under a N2 atmosphere for 30 s using a rapid thermal annealing process. The composition and thickness of HZO films were examined using X-ray fluorescence spectroscopy (Quant’X,

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| In this paper, therefore, the experimental data (grain size | Thermo | Scientific) | and | ellipsometry | (L-116d, | Gaertner), |

distribution, phase evolution and ferroelectric properties) for Hf1−xZrxO2 thin films of various compositions (x = 0, 0.19, 0.43, 0.70, and 1.00) and thicknesses (9.2, 14.2, 19.2, 24.2, and 29.2 nm) are carefully examined and compared with the theoretical expectation based on the previous computational calculation for the same material system by Materlik et al.42 Most of the experimental data were taken from Park’s disser-tation,50while the thermodynamically stable phases were cal-culated based on the thermodynamic surface energy model in

9974 | Nanoscale, 2017, 9, 9973–9986

respectively. Since the film thickness of HZO films could not be directly measured on the TiN bottom electrode, the linear relationship between the areal atomic density and film thick-ness of HZO films on the Pt electrode and the Si substrate was first verified. From the linear relationship, the thickness of HZO films could be estimated from the layer density measured using XRF. It was confirmed that the thickness estimated from the layer density is consistent with the thickness from cross-sectional transmission electron microscopy (TEM) images in

This journal is © The Royal Society of Chemistry 2017

**[View Article Online](http://dx.doi.org/10.1039/C7NR02121F)** Nanoscale Paper

our previous studies.19,34,35,52Polarization–voltage and capaci-tance–voltage characteristics were measured using a ferroelec-tric tester (TF analyzer 2000, Aixacct Systems) and an impe-dance analyser (4194A, HP) at a frequency of 1 and 10 kHz, respectively. The AC voltage amplitude used for capacitance–voltage characterization was 50 mV. The microstructure of the films was analysed using field emission SEM (SU70, Hitachi,

were the lowest whereas the m-phase showed the highest values. The Gbulk and γs of the o-phase are in between those of the m- and t-phases. Therefore, the stable phase changes from the m-phase in the bulk to the t-phase when the grain size is decreased, but the o-phase can be stabilized within a certain range of grain size during the transition between the m- and t-phases. Accordingly, the critical grain radius (rcrit,x−y) where

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 7 03:33:50. | or S4800, Hitachi). For crystal structural analysis, a grazing | | | | | | | | | | the total free energy of x- and y-phases is equivalent (x and y | | | | | | | | | | | |
| incidence X-ray diffraction (GIXRD) analysis was conducted | | | | | | | | | | can be the t-, o-, or m-phases) can be calculated using eqn (2). | | | | | | | | | | | |
| using | an | X-ray | diffractometer | | (X’Pert | | Pro, | | Panalytical) | rcrit;x�y ¼ �ΔGbulk;x�y 2Δγgb;x�y | | | | | | 1 | Δγif;x�y | !�1 | | ; | ð2Þ |
| equipped with a Cu Kα X-ray source. For GIXRD measure- | | | | | | | | | |
| Published on 14 June 2017. Downloaded by Georgia Institute of Technology on 11/11/201 | ments, the incidence angle was fixed at 0.5°, and a 2θ scan was | | | | | | | | | | þ | Δγgb;x�y |  |
| conducted. A grain size distribution analysis was conducted | | | | | | | | | |
| where ΔGbulk,x−y, and Δγx−y refer to the bulk free energy differ- | | | | | | | | | | | |
| using the watershed method implemented in the Gwyddion | | | | | | | | | |
| software. | | | | | | | | | | ence between x- and y-phases, and the surface energy differ- | | | | | | | | | | | |
| ence between x- and y-phases, respectively. Using eqn (2), the | | | | | | | | | | | |
| Results and discussion | | | | | | | | | | range of lateral grain sizes for each phase can be easily calcu- | | | | | | | | | | | |
| lated. Therefore, with a distribution of the lateral grain size of | | | | | | | | | | | |
| the samples, the most probable phase distribution can be | | | | | | | | | | | |
| Surface energy model | | | | | | | | | | obtained by estimating the most stable phase for each grain | | | | | | | | | | | |
| In this section the model proposed in ref. 42 will be briefly | | | | | | | | | | with a different size. | | | | | | | | | | | |
| reviewed. As previously mentioned, Materlik et al.42suggested | | | | | | | | | | Experimental data | | | | | | | | | | | |
| that the stabilization of the metastable ferroelectric phase can | | | | | | | | | |
| be understood based on the surface energy effect. According to | | | | | | | | | | Electrical properties. Fig. 1 shows the polarization–electric | | | | | | | | | | | |
| their model, the free energy of each phase in grains can be cal- | | | | | | | | | | field | (P–E) | curves | of | HfO2, | Hf0.81Zr0.19O2, | | | | Hf0.57Zr0.43O2, | | |
| culated based on the bulk free energy, surface energy, lateral | | | | | | | | | | Hf0.30Zr0.70O2, and ZrO2 films of various thicknesses (9.2, 14.2, | | | | | | | | | | | |
| dimensions of grains, and film thickness. From experiments | | | | | | | | | | 19.2, 24.2, and 29.2 nm) sandwiched between a Pt/TiN top | | | | | | | | | | | |
| columnar grains that span the whole film thickness are | | | | | | | | | | electrode (where the TiN layer is in contact with the dielectric | | | | | | | | | | | |
| expected in doped HfO2 thin films.7For the sake of conven- | | | | | | | | | | layer) and a TiN bottom electrode. The P–E characteristics were | | | | | | | | | | | |
| ience, | cylindrical-shaped | | | grains | with | identical | | | size were | taken from the dissertation by Park.50All the samples used for | | | | | | | | | | | |
| assumed. Then, the free energy of a grain with lateral radius | | | | | | | | | | the electrical characterization were annealed at 500 °C under a | | | | | | | | | | | |
| r and film thickness t was calculated using eqn (1): | | | | | | | | | | N2 atmosphere for 30 s (post metallization annealing, PMA) | | | | | | | | | | | |
| Ggrain ¼ Gbulk þ2πr2γif þ 2πrtγgb | | | | | | | | ; | ð1Þ | after the formation of the top electrode. The fabrication pro- | | | | | | | | | | | |
| cesses of capacitors are explained in detail in the Experimental | | | | | | | | | | | |
| section. The variation in the P–E curves with the cation compo- | | | | | | | | | | | |
| where Ggrain, Gbulk, γif and γgb are the free energy per unit | | | | | | | | | | sition of 9.2 nm-thick HZO films was almost identical to the | | | | | | | | | | | |
| volume of the grain, the free energy per unit volume of the | | | | | | | | | | results previously reported by Müller et al.;20the Hf0.57Zr0.43O2 | | | | | | | | | | | |

bulk, the interface energy (the metal/oxide interface in the metal–HfO2–metal capacitor structure) and the grain boundary energy, respectively. These parameters are dependent on the film composition, and can be calculated from values reported for HfO2, Hf0.5Zr0.5O2, and ZrO2 based on Vegard’s law. In ref. 42 the γif and γgb values were assumed to be identical to the surface energy, which could be problematic. This hypothesis arises from the calculation based on the nanoscale crystallites, sandwiched between the top and bottom electrodes rather than the grains in polycrystalline films. Hence, reasonable assumptions for the interface energy and grain boundary energy are required to calculate the free energy of crystalline phases in polycrystalline thin films. This will be discussed in more detail in sections 3 and 4.

From eqn (1), the total free energies of each phase for a specific size of the grains can be easily calculated under the given hypothesis. According to ref. 42, Gbulk of the m-phase was the lowest whereas that of the t-phase was the highest. In the case of the surface energy (γs), the values of the t-phase

This journal is © The Royal Society of Chemistry 2017

films with a thickness of 9.2 nm show a robust ferroelectricity with a doubled remanent polarization (2Pr) of 33 μC cm−2. The 2Pr value decreases with increasing Zr or Hf contents. On increasing the Hf-concentration, the 2Pr value monotonically decreases, while the films with higher Zr-concentration show antiferroelectric-like properties before they become linearly dielectric for pure ZrO2. For 9.2 nm-thick ZrO2 films it is believed that an even higher electric field would be required to induce the ferroelectric o-phase. However, such a high electric field could not be applied since the breakdown field is lower. It seems that the electric field required for the transition to the o-phase decreases with increasing film thickness for pure ZrO2 due to the surface energy effect. While a previous report by Müller et al.20did not report on the thickness effect, Fig. 1 clearly reveals that the film thickness plays a role as important as composition for the occurrence of ferroelectricity. For the Hf0.57Zr0.43O2 films, 2Pr remains almost constant when the thickness of the film is below 20 nm, but decreases rapidly when the thickness is above 25 nm. Other films with slightly

Nanoscale, 2017, 9, 9973–9986 | 9975

**[View Article Online](http://dx.doi.org/10.1039/C7NR02121F)**

|  |  |  |
| --- | --- | --- |
| Published on 14 June 2017. Downloaded by Georgia Institute of Technology on 11/11/2017 03:33:50. | Paper | Nanoscale |
| Fig. 1 |  |
| Polarization–electric field (P–E) curves of Hf1−xZrxO2 films with various compositions (x = 0.00, 0.19, 0.43, 0.70, 1.00) and thicknesses (∼9.2, |

14.2, 19.2, 24.2, and 29.2 nm).

higher or lower Zr-concentration show similar variations with thickness. The variation of the dielectric constant εr with thick-ness and composition was examined by capacitance–voltage (C–V) analysis, and the dielectric constant–electric field (εr–E) curves are included in Fig. S1 of the ESI.† The changes in the εr–E characteristics matched well with the changes in P–E

films using the software Gwyddion.51Fig. 3a–e show the grain size distribution of HZO films when x is 0.00, 0.19, 0.43, 0.70, and 1.00, respectively. It should be noted that the grain size analysis was conducted on the SEM images from PDA samples instead of PMA samples. To confirm the effects of the TiN capping layer on the grain sizes and their distributions, the

characteristics. grain size distributions of ∼9.1 nm-thick Hf0.48Zr0.52O2 films

Physical properties. Fig. 2 shows the plane-view SEM images of HZO films with various x-values of film composition and film thicknesses which were also taken from the dissertation by Park.50It can be noticed from Fig. 2 that the grain size dis-tribution is composition dependent. Especially for the films thicker than 19.2 nm, the grain sizes of higher Hf-concen-tration films were larger than those of higher Zr-concentration films. The grain size distribution was examined for the HZO

9976 | Nanoscale, 2017, 9, 9973–9986

annealed with PMA and PDA were compared after removing the TiN capping layer by a wet etching process. It could be con-cluded that the effect of the upper TiN capping layer on the grain size distribution was negligible. The plane-view SEM images and the grain size distribution of PMA and PDA Hf0.48Zr0.52O2 thin films are given in Fig. S2 in the ESI.† It is known that the grain size estimated from SEM images can be different from the crystallographic grain size which can be

This journal is © The Royal Society of Chemistry 2017

**[View Article Online](http://dx.doi.org/10.1039/C7NR02121F)**

|  |  |  |  |
| --- | --- | --- | --- |
| Published on 14 June 2017. Downloaded by Georgia Institute of Technology on 11/11/2017 03:33:50. | Nanoscale | | Paper |
|  | | |
| Fig. 2 | Planar scanning electron microscopy images of Hf1−xZrxO2 films with various compositions (x = 0.00, 0.19, 0.43, 0.70, 1.00) and thicknesses | |
| (∼9.2, 14.2, 19.2, 24.2, and 29.2 nm). | | |

extracted from TEM investigations. However, for HZO thin films, it was confirmed that the grain size from SEM images is similar to that from TEM in a previous study.19The median grain size increases with increasing film thickness when x = 0.00, 0.19, and 0.43, whereas it remains almost constant when x = 0.70 and 1.00. On varying the thickness of HZO films with x = 0.70 and 1.00, there are slight differences in the grain size distribution, but the median grain size does not increase with increasing film thickness.

The difference in thickness dependence of grain size distri-butions is believed to be related to the different crystallization behaviours. It is well known that the crystallization tempera-ture of HfO2 is higher than that of ZrO2, and in thin films it is also affected by the film thickness.53Therefore, the GIXRD patterns of H1−xZrxO2 films after the film deposition (black curves) and those after the PMA (red curves) were compared. Fig. 4a–e show the GIXRD patterns of HZO films with x = 0.00, 0.19, 0.43, 0.70, and 1.00, respectively, analysed before and

This journal is © The Royal Society of Chemistry 2017

after the PMA. As expected from the crystallization tempera-ture of HfO2 and ZrO2, the in situ crystallization during the ALD process was enhanced with increasing x value when the film thickness is fixed. On increasing the film thickness, the in situ crystallization also increased, which also well matches with the general trend of these thin films.53For the quantitat-ive comparison, the degree of crystallization in the as-deposited state was estimated by semi-quantitative compari-son of the GIXRD patterns before and after PMA. For that purpose, the diffraction patterns within a 2θ range of 27–33 degrees were taken. The area of the diffraction peak from the 111 and −111 planes of the m-phase and that from the 111 plane of the o-phase or the 011 plane of the t-phase were cal-culated and the results are summed up. Although the precise identification of the XRD peaks from these thin films is regarded as challenging since a precise and detailed assign-ment of each peak is still unavailable, this approach is gener-ally accepted in the community. The total area of the afore-

Nanoscale, 2017, 9, 9973–9986 | 9977

**[View Article Online](http://dx.doi.org/10.1039/C7NR02121F)**

|  |  |  |  |
| --- | --- | --- | --- |
| Downloaded by Georgia Institute of Technology on 11/11/2017 03:33:50. | Paper | | Nanoscale |
|  | | |
| Fig. 3 | Grain size distribution of (a) HfO2, (b) Hf0.81Zr0.19O2, (c) Hf0.57Zr0.43O2, (d) Hf0.30Zr0.70O2, and (e) ZrO2 thin films analysed using the watershed | |
| method implemented in the Gwyddion software. | | |
| Published on 14 June 2017. |  | | |
| Fig. 4 | Grazing incidence X-ray diffraction (GIXRD) patterns of (a) HfO2, (b) Hf0.81Zr0.19O2, (c) Hf0.57Zr0.43O2, (d) Hf0.30Zr0.70O2, and (e) ZrO2 thin films | |

with film thicknesses of 9.2, 19.2, and 29.2 nm (black: as-deposited, red: annealed at 500 °C for 30 s under a N2 atmosphere). (f) Three-dimensional surface plot for the crystallinity of as-deposited films calculated by comparing the GIXRD patterns of as-deposited and annealed films.

9978 | Nanoscale, 2017, 9, 9973–9986

This journal is © The Royal Society of Chemistry 2017

**[View Article Online](http://dx.doi.org/10.1039/C7NR02121F)** Nanoscale Paper

mentioned diffraction peaks calculated from the GIXRD pat-terns before PMA was divided by that after PMA. While such analysis cannot give a quantitative estimation of the crystalli-nity of the as-deposited film, this can be taken as a useful assessment of the relative degree of crystallization of the as-deposited film. The resulting degree of crystallinity is plotted as a surface map in Fig. 4f, revealing that the crystallinity of

Comparison of the theoretical model and experiments   
Fig. 5a shows the three dimensional surface plot of 2Pr values taken from the P–E curves in Fig. 1 (after PMA). It is important to compare the data with the evolution of the crystallographic phases. This electrical performance map could be compared with the theoretically estimated phase change, especially the

|  |  |  |  |
| --- | --- | --- | --- |
| loaded by Georgia Institute of Technology on 11/11/2017 03:33:50. | the as-deposited films increases with increasing x value and | | o-phase, shown in Fig. 5b, where the o-phase fraction was cal- |
| film thickness. In fact, the GIXRD pattern of the as-deposited | | culated based on the aforementioned thermodynamic model |
| ZrO2 film was almost identical to that of the film after PMA. | | using the grain size distribution shown in Fig. 3. The phase |
| Therefore, the different grain size distributions for the Hf-rich | | evolution could have been alternatively examined by using |
| and Zr-rich films shown in Fig. 2 and 3 can be understood as | | GIXRD patterns as conducted in a previous study.21However, |
| follows. For the Hf-rich film, the as-deposited films are mostly | | this method was not adopted because determining lattice |
| amorphous, and thus crystallization was induced by the PMA, | | parameters of HZO films with various Zr-concentrations using |
| which resulted in the rather broad and non-uniform distri- | | GIXRD is a challenging task. The composition dependence of |
| bution of the grain size. Consequently, the ferroelectric pro- | | lattice parameters of the crystalline phases and the effect of |
| perties of the HfO2 thin films become further degraded in thicker films. In contrast, for the Zr-rich film, the as-deposited | | film stress, which also has a non-negligible influence, cannot be accurately considered in such an analysis.21Nonetheless, |
| film already contains a rather high fraction of crystalline phase which may play the role of uniform crystalline nuclea- | | Schenk examined the stress in Si-doped HfO2 film using the sin2Ψ method, and 1.5–2 GPa of tensile stress could be |
| tion and growth sites of the remaining amorphous material | | measured.54However, such detailed X-ray analyses were not |
| during the PMA. The initially uniform crystalline seeds | | attempted in this work. Fig. 5b shows a three dimensional |
| induced a uniform grain size distribution, which has an | | surface plot of the relative o-phase fractions in HZO films with |
| important implication for the film performance. | | x = 0.0, 0.19, 0.43, 0.70, and 1.00 at 300 K. It was assumed that |
| Published on 14 June 2017. Down |  | | |
| Fig. 5 | Three-dimensional surface plot of (a) experimental double remanent polarization (2Pr) and orthorhombic phase (o-phase) fraction expected | |

from the surface energy model for Hf1−xZrxO2 films with the assumption that (b) γgb = γs and (c) γgb = 0.33γs for various compositions (Zr/[Zr + Hf] = 0.00, 0.19, 0.43, 0.70, 1.00) and thicknesses (∼9.2, 14.2, 19.2, 24.2, and 29.2 nm). (d) o-Phase fraction expected for HZO films when the role of TiN upper capping layers was considered.

This journal is © The Royal Society of Chemistry 2017

Nanoscale, 2017, 9, 9973–9986 | 9979

**[View Article Online](http://dx.doi.org/10.1039/C7NR02121F)** Paper Nanoscale

the plane-view image of a 9 nm thick sample processed under similar conditions to those given in ref. 19 mimics the results

Possible reasons for discrepancies between the surface energy model and experimental conclusions

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Published on 14 June 2017. Downloaded by Georgia Institute of Technology on 11/11/2017 03:33:50. | of the 9.2 nm films investigated here, since their deposition | Stress in thin films. To understand the aforementioned dis- | | | | | | | |
| processes were identical. Changes in the relative fractions of |
| crepancies between the experimental results and the expec- | | | | | | | |
| all the m-, o- and t-phases in HZO films with various Zr con- |
| tation from the thermodynamic surface energy model, various | | | | | | | |
| tents are plotted in Fig. S3 of the ESI.† It was assumed that the |
| factors should be considered. Among them, film stress from | | | | | | | |
| difference in the grain size distribution between HfO2 and |
| various sources must be heavily considered. Park et al. exam- | | | | | | | |
| ZrO2 is negligible in films with 9.2 nm thickness after PMA. |
| ined in detail the effect of film strain on the ferroelectric pro- | | | | | | | |
| Two significant differences between the experimental 2Pr |
| perties of Hf0.5Zr0.5O2 thin films.23They used the 111 peak | | | | | | | |
| values and the theoretically calculated o-phase fractions could |
| position of the o-phase of their GIXRD spectra as a strain | | | | | | | |
| be noticed when comparing Fig. 5a and b. First, the compo- |
| gauge, and suggested that about 1.5% tensile strain is required | | | | | | | |
| sition and film thickness at which the 2Pr value is the highest |
| to induce the o-phase from the t-phase.21,23Shiraishi et al. | | | | | | | |
| in Fig. 5a and that where the o-phase fraction is the highest in |
| examined the effects of the coefficient of thermal expansion | | | | | | | |
| Fig. 5b are different. The experimental 2Pr value was the |
| on the o-phase formation and concluded that a large tensile | | | | | | | |
| largest at Hf0.57Zr0.43O2 composition for all film thicknesses, |
| stress is favourable for the o-phase formation whereas it is | | | | | | | |
| whereas from the theoretical estimation, the Hf0.30Zr0.70O2 |
| unfavorable for the m-phase formation.56Schenk examined | | | | | | | |
| film is expected to have the highest o-phase fraction when the |
| the film stress in Si-doped HfO2 thin films using the sin2Ψ | | | | | | | |
| film thickness is thicker than 14.2 nm. It seems that this dis- |
| method. The estimated film stress (σfilm) was approximately | | | | | | | |
| crepancy is related to the in situ crystallization during the ALD |
| 1.5–2 GPa.54When the similar mechanical properties of HfO2 | | | | | | | |
| process which has already been presented in Fig. 4 and the |
| and ZrO2 are considered, the film strain in an HZO film | | | | | | | |
| related text. Second, the critical thickness at which 2Pr |
| should also be similar to that of a Si-doped HfO2 thin film. Based on their theoretical calculations42reported, the bulk | | | | | | | |
| abruptly decreases is quite different from the critical thickness |
| at which the o-phase fraction is reduced. The experimental 2Pr |
| modulus (K) of the t-, o-, and m-phase for Hf0.5Zr0.5O2 was | | | | | | | |
| value of the 19.2 nm-thick Hf0.57Zr0.43O2 film is 29.5 μC cm−2, |
| found to be 210 GPa, 224 GPa and 185 GPa, respectively. | | | | | | | |
| which rapidly decreases with increasing thickness above |
| Young’s modulus (Y) can be calculated from K and the | | | | | | | |
| 24.2 nm. From the theoretical expectation, however, the |
| Poisson’s ratio ν according to the equation Y = 3K(1 − 2ν). For | | | | | | | |
| o-phase fraction of the 9.2 nm-thick Hf0.57Zr0.43O2 film is as |
| fluorite-structured | ceramic | materials | | it | is | a | reasonable |
| high as 88%, and drastically decreases to 41% only when the |
| assumption to set ν equal to 0.3 for all phases.57Then the Y of | | | | | | | |
| film thickness increases to 14.2 nm. This result implies that in |
| the t-, o-, and m-phases can be calculated as 252 GPa, 269 GPa | | | | | | | |
| actual experiments, the m-phase formation in Hf0.57Zr0.43O2 |
| and 222 GPa. With these results, the elastic strain energy | | | | | | | |
| films is much more deterred than theoretically expected at a |
| (Eelastic) in the thin film can be calculated using: | | | | | | | |
| given thickness. |
| It should be noted that Fig. 5b was plotted based on the | Eelastic ¼1 � ν | | | σfilm | 2 | ð3Þ | | |
| assumption that ‘γgb = γif = γs’ which was the first suggestion in the original paper on the surface energy model.42It is, |
| however, known that the γgb of high-angle (between the two | From eqn (3), the calculated Eelastic values of the t-, o-, and m-phases under a film stress of 2 GPa are 2.3 meV f.u.−1, | | | | | | | |
| crystallographic orientations of the involved grains) incoherent |
| grain boundaries is approximately 1/3 of γs.55Schenk exam- | 2.2 meV f.u.−1, and 2.7 meV f.u.−1, respectively. The differences | | | | | | | |
| ined the texture of Si-doped HfO2 films in his dissertation, and no strong preferred orientation could be found.54Therefore, | between them are smaller than 0.5 meV f.u.−1, which is rather | | | | | | | |
| small to explain a significant influence on the phase evolution | | | | | | | |

the assumption of a high angle grain boundary, where the orientation difference between two adjacent grains is larger than 15 degrees, is believed to be reasonable. From eqn (2), it can be noticed that the critical lateral grain size is proportional to γgb. Therefore, the assumption that ‘γgb = 1/3γs’ will signifi-cantly decrease the resulting critical lateral grain size, implying that the results for the relative fraction of the t- and o-phase should also decrease. Fig. 5c shows a similar plot of the o-phase fraction with the assumption that ‘γgb = 1/3γs’, showing a significantly decreased relative o-phase portion compared to Fig. 5b. Nonetheless, the emergence of the highest fraction of the o-phase at x ∼ 0.7 is still evident even under this assumption for the calculation. The changes in the relative fractions of all the m-, o- and t-phases in HZO films with various Zr contents based on the assumption that ‘γgb = 1/3γs’ are plotted in Fig. S4 of the ESI.†

9980 | Nanoscale, 2017, 9, 9973–9986

in this material system. Next, the effect of capping by TiN is considered as a root cause for discrepancies between the surface energy model and experimental results.

Effect of upper TiN capping layers. In previous studies, upper TiN capping layers were reported to strongly affect the evolution of polymorphism of doped HfO2 thin films.5,9 Mueller et al. suggested that the TiN capping layer prevents the shear strain which induces the phase transformation from the t- to m-phase during cooling.9It was also suggested that the upper TiN capping layer prevents the surface diffusion, and the subsequent grain growth and accompanying transform-ation to the m-phase can be suppressed.27Toriumi et al. exam-ined the effect of the Si upper capping layer on the kinetics of the phase transition from a metastable tetragonal or cubic phase to the monoclinic phase.58They reported that the Si upper capping layer significantly increased the activation

This journal is © The Royal Society of Chemistry 2017

**[View Article Online](http://dx.doi.org/10.1039/C7NR02121F)** Nanoscale Paper

energy for a monoclinic phase formation, so the Si capping layer could kinetically suppress the monoclinic phase for-mation.58Based on the aforementioned reports, it is believed that the TiN capping layer is also expected to affect the kinetic energy barrier for the monoclinic phase formation. Thus, the effect of the TiN capping layer (the top electrode, in this case) must be taken into consideration because the HZO films were

maximum of the o-phase fraction is still observed at a compo-sition x of about 0.7. Therefore, the effect of the TiN capping cannot fully explain the experimental results.

Influence of partial crystallization of as-deposited films. The theoretical estimation of the phase evolution shown in Fig. 5b actually corresponds to a circumstance where an initially uniform amorphous material is crystallized to a polycrystalline

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Published on 14 June 2017. Downloaded by Georgia Institute of Technology on 11/11/2017 03:33:50. | annealed at 773 K with the TiN top electrode being deposited. | | | | | | | | material with different grain size distributions and accordingly |
| To understand the effect of the TiN capping layer, the crys- | | | | | | | | different phases. However, this is certainly different from what |
| tallization process at 773 K and subsequent cooling down to | | | | | | | | actually is happening during the experiment. As can be under- |
| 300 K need to be understood. According to previous studies, | | | | | | | | stood from the GIXRD patterns of the as-deposited films, the |
| the crystalline phase formed during the crystallization anneal- | | | | | | | | Zr-rich films are already significantly crystallized, and Hf-rich |
| ing process is most probably the t-phase before cooling down, | | | | | | | | films also have a certain crystallinity but a lower degree of crys- |
| whereas large grains are still in an m-phase. But at this temp- | | | | | | | | tallization compared to the Zr-rich films. In detail, the in situ |
| erature almost no o-phase is present, which was confirmed by | | | | | | | | crystallization of the ALD films is quite different from the |
| high temperature XRD studies.9Such a stabilization of the | | | | | | | | aforementioned crystallization during PMA, because in situ |
| t-phase at high temperature can be understood from the | | | | | | | | crystallization is mainly induced by the two-dimensional |
| entropy effect (G = H − TS, where G, H, and S are the Gibb’s | | | | | | | | migration of adsorbing atoms on the film surface.59In con- |
| free energy, enthalpy, and entropy, respectively). Due to its | | | | | | | | trast, the crystallization by PMA proceeds via the classical |
| higher entropy compared to those of the m- and o-phases, the | | | | | | | | solid-state phase transition. The complicated surface reactions |
| t-phase can be stabilized during crystallization annealing at | | | | | | | | between the adsorbing chemicals (the metal precursor, the |
| 773 K within a very wide grain size region.42During cooling | | | | | | | | oxygen source, the film surface during steady-state growth, or |
| down to room temperature, however, the entropy effect | | | | | | | | the substrate during initial nucleation) also largely influence |
| becomes mitigated and the t-phase should be partially trans- | | | | | | | | the in situ crystallization.60Nonetheless, when the deposited |
| formed to the m-phase or o-phase. In fact, the data shown in | | | | | | | | film is partially crystalline, the evolution of the crystalline |
| Fig. 5c correspond to the situation where, besides the bulk | | | | | | | | phase from the remaining amorphous material should be |
| and grain boundary energies, no other constraints on the | | | | | | | | affected by the already crystallized fraction. It is highly prob- |
| phase evolution are involved during cooling down after PMA. | | | | | | | | able that the crystallization of the amorphous part of the as-de- |
| This may not be the case in the actual experiment. | | | | | | | | posited film proceeds via the heterogeneous nucleation and |
| The influence of the TiN capping layer on the phase evol- | | | | | | | | growth from the already-present crystalline part. Their size is |
| ution is considered to be as follows. First, the grain size distri- | | | | | | | | expected to be much smaller than the estimated grain size |
| butions at 773 K for the samples at all compositions are | | | | | | | | after the PMA (Fig. 2 and 3). Under these circumstances, the |
| assumed to be identical to Fig. 3. This assumption may be | | | | | | | | identification of the crystalline phase of the as-deposited film |
| slightly incorrect due to the fact that the TiN capping would | | | | | | | | is critically important since it will influence the final crystalli- |
| suppress | the | grain | growth | by | suppressing | the | surface | zation phases. However, to precisely identify such small crys- |
| diffusion. However, it was assumed that the grain growth | | | | | | | | talline phases using GIXRD (even when a synchrotron X-ray |

during cooling down after annealing process is negligible. According to the thermodynamic data at 773 K the phase dis-tribution under each condition can be calculated. Accordingly, the films are expected to be composed of mostly m- and t-phases at 773 K. During cooling down, relatively large t-phase grains can (partially) transform to the o- or m-phase, whereas sufficiently small grains still exist in t-phase even at 300 K. The critical grain radius range for such phase transitions can be calculated based on the surface energy model. However, the TiN capping can suppress the transformation from the t-phase to the m-phase. Therefore, the fraction of grains that are sup-posed to be in the m-phase are now assumed to be in the o-phase. Only the amount of the m-phase formed at 773 K was considered to remain after cooling down to 300 K. Fig. 5d shows the o-phase fraction calculated according to this pro-cedure. The changes in the relative fractions of the m-, o- and t-phases in HZO films with various Zr contents based on the assumptions ‘γgb = 1/3γs’ and the described TiN capping effect are plotted in Fig. S5 of the ESI.† While the o-phase fraction is significantly increased compared to the results of Fig. 5c, the

This journal is © The Royal Society of Chemistry 2017

source is applied) is extremely challenging.27Therefore, the aforementioned theoretical prediction is revisited. For this purpose, first the grain size must be determined. Fortunately this can be accomplished using the detailed XRD pattern.

From Fig. 4f, the degrees of crystallization of the 9.2 nm-thick Hf0.57Zr0.43O2 and Hf0.30Zr0.70O2 films were 11 and 23%, and the values for 19.2 nm-thick films were 84 and 88%, respectively. Therefore, the 9.2 nm-thick films were considered to be partially crystalline films, and their GIXRD patterns were used to analyse the crystallization process. For the as-deposited 9.2 nm-thick Hf0.57Zr0.43O2, Hf0.30Zr0.70O2, and ZrO2 films, weak and broad o111/t101 peaks can be observed in Fig. 4c–e. The broadening of the diffraction peaks can be related to the small size of the crystallites, and the Scherrer equation can be used to estimate the crystallite size.61To pre-cisely estimate the peak broadening effect from small crystal-lites, the broadening from other factors needs to be excluded. For this purpose, the broadening of a diffraction peak of single crystalline MgO and Si substrates was measured, and the broadening of the substrate peak (the full width at half

Nanoscale, 2017, 9, 9973–9986 | 9981

**[View Article Online](http://dx.doi.org/10.1039/C7NR02121F)** Paper Nanoscale

maximum, FWHM, is 0.07°) turned out to be less than 5%, compared to that of the o111/t101 diffraction peak of HZO (x = 0.43, 0.70, and 1.00) films with a FWHM in the range of 1.8 to 2.4°. Thus, the broadening from other effects than the size can be ignored. By applying the Scherrer equation, the crystallite

present in the as-deposited film retain their crystalline struc-ture after the PMA and, furthermore, play the role of a hetero-geneous nucleation site for the subsequent crystallization of the remaining amorphous material during the PMA. This result is consistent with the achieved electrical properties from

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Published on 14 June 2017. Downloaded by Georgia Institute of Technology on 11/11/2017 03:33:50. | sizes | of | the | as-deposited | 9.2 | nm-thick | Hf0.57Zr0.43O2, | the annealed 9.2 nm-thick films: a Hf0.57Zr0.43O2 film was fer- | | | | | | | | |
| Hf0.30Zr0.70O2, and ZrO2 films were estimated to be in the | | | | | | | roelectric while annealed Hf0.30Zr0.70O2 and ZrO2 films were | | | | | | | | |
| range of 3.5 to 4.5 nm. No trend was observed for the variation | | | | | | | antiferroelectric-like or even dielectric. | | | | | | | | |
| of the Zr-concentration. The calculations are in fair agreement | | | | | | | Finally, the difficulties of the emergence of ferroelectricity | | | | | | | | |
| with those from previous studies.62–64Although the degree of | | | | | | | in undoped HfO2 and ZrO2 are discussed within the context of | | | | | | | | |
| crystallization of as-deposited films was different for films | | | | | | | previous discussions. For HfO2 thin films, the crystallite | | | | | | | | |
| with different Zr-concentrations, the crystallite size turned out | | | | | | | radius | range | for | the | o-phase | formation | is | 0.8–1.3 | and |
| to be almost identical. These crystallites in the as-deposited | | | | | | | 0.5–0.8 nm with the assumption of γif = 0.5γs and γif = 0.33γs, | | | | | | | | |
| film have an effect on the evolution of the polymorphism in | | | | | | | respectively. Being even smaller than 3 unit cells, these values | | | | | | | | |
| the annealed HZO films. | | | | | | | are unreasonably small compared to the previous experimental | | | | | | | | |
| Another parameter necessary for calculating the total free | | | | | | | reports.62–64Bohra et al. reported that the nuclei of HfO2 thin | | | | | | | | |
| energy is the γif between crystallites and the amorphous | | | | | | | films had cylindrical shape with a diameter of 5 nm and a | | | | | | | | |
| matrix. It is difficult to estimate this value precisely. However, | | | | | | | thickness of 2 nm in a 2 nm-thick HfO2 thin film.62To the | | | | | | | | |
| as in the case of γgb, it will be slightly smaller than γs. | | | | | | | authors’ knowledge this is the smallest grain size reported so | | | | | | | | |
| Therefore, to roughly estimate the γif effect, γif was assumed to be in the range from 1/3γs to 1/2γs.55,65With the assumption | | | | | | | far. In the classical crystallization theory, there is a critical size | | | | | | | | |
| of the crystallite below which the temporarily formed crystal- | | | | | | | | |
| that the shape of the crystallites is spherical, the relative Gibbs | | | | | | | line embryos disappear since the decrease in bulk free energy | | | | | | | | |
| free energy ΔG of the tetragonal and orthorhombic crystallites | | | | | | | due to crystallization is lower than the increased interfacial | | | | | | | | |
| can be calculated by setting the free energy of the monoclinic | | | | | | | energy.65It was assumed that the critical grain size of HfO2 is | | | | | | | | |
| crystallite to zero. Fig. 6a and b show the calculated results | | | | | | | larger than the size required for the o-phase formation. | | | | | | | | |
| with the assumption of γif = 1/3γs and γif = 1/2γs, respectively. | | | | | | | However, this does not necessarily mean that inducing ferro- | | | | | | | | |
| As can be readily expected, the negative ΔG values in Fig. 6a | | | | | | | electricity in undoped HfO2 is impossible. Polakowski et al. | | | | | | | | |
| and b show that the orthorhombic and tetragonal crystallites | | | | | | | reported the emergence of ferroelectricity in undoped HfO2 | | | | | | | | |
| are more stable than the monoclinic ones. Interestingly, for | | | | | | | films deposited by ALD.8In that report, it was suggested that | | | | | | | | |
| both cases, the stability of the t-phase increases with increas- | | | | | | | the ferroelectricity could be induced by the surface energy | | | | | | | | |
| ing Zr-concentration. However, close to a Zr-concentration of | | | | | | | effect, but they took the surface energy as the grain boundary | | | | | | | | |
| 50% the o-phase shows higher stability. This is certainly in | | | | | | | energy, which surely overestimated the grain boundary effect.42 | | | | | | | | |
| contradiction to the theoretical estimation shown in Fig. 5c | | | | | | | Kim et al. could induce ferroelectric properties in nominally | | | | | | | | |
| which was built based on the grain size extracted from the | | | | | | | undoped HfO2 thin films by decreasing the deposition temp- | | | | | | | | |
| films after PMA. From Fig. 5c, the most stable phase for a Zr- | | | | | | | erature of the ALD process. However, they observed increased | | | | | | | | |
| concentration close to 50% was the m-phase and that for a Zr- | | | | | | | impurity such as C and N in their films.19The role of such | | | | | | | | |

concentration around 70% was the o-phase. In Fig. 6 the o-phase appears to be more stable around 50% and the t-phase is more stable around 70%. These o- and t-phases

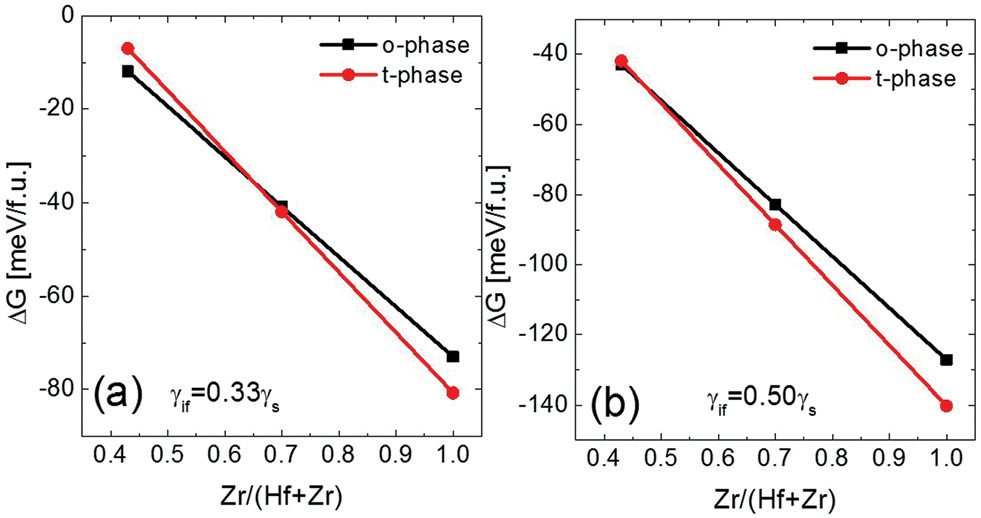


Fig. 6 Relative free energy of orthorhombic and tetragonal crystallites

as a function of Zr content with the assumption of (a) γif (interface energy) = 0.33γs (surface energy) and (b) γif = 0.50γs (o-phase: ortho-rhombic phase, t-phase: tetragonal phase).

9982 | Nanoscale, 2017, 9, 9973–9986

impurities in HfO2 thin films has not yet been clearly under-stood. Nonetheless, Xu et al. reported that N doping can induce ferroelectricity in HfO2 thin films.17These reports show that the o-phase can be formed in nominally undoped

HfO2, but it cannot be understood solely as a size effect. Pal et al. reported that decreasing the ozone dose time for the

HfO2 ALD process could increase the oxygen vacancy concen-tration and also increase the Pr value of the undoped 8 nm-thick HfO2 film, and this result matched well with the previous computational calculation results.66 Consequently, it is

believed that ferroelectricity can be induced in undoped HfO2, but it might need additional factors other than the size effect.

For ZrO2 thin films, no crystallite radius range for the o-phase stabilization is expected, suggesting that the ortho-

rhombic crystallite is very difficult to form due to the interface

energy effect alone. This might be due to the large bulk free

energy difference between the o- and t-phases that has to be

overcome solely by the interface energy effect. Therefore, to

induce ferroelectric properties in pure ZrO2 thin films, factors other than the size effect will be required. Fan et al. reported

This journal is © The Royal Society of Chemistry 2017

**[View Article Online](http://dx.doi.org/10.1039/C7NR02121F)**

|  |  |
| --- | --- |
| Nanoscale  the emergence of a temporary ferroelectric property in 111-tex-tured ZrO2 thin films, but it disappeared when the electric field increased above a certain critical value.25In that paper, | Paper  Electrical performance diagram according to the composition and thickness |

they suggested that compressive strain along the <11−2> direc-tion can temporarily stabilize the o-phase.25Lin et al. also

reported that in situ annealed ALD ZrO2 thin films on a Pt elec-trode could show ferroelectricity.67Starschich et al. reported

Fig. 7 shows the variations in the dielectric behaviour of the HZO films with different compositions and thicknesses. Details of the electrical data of each data point are reported elsewhere,21,23,34,35,50,68,69and the characteristic P–E curves are

|  |  |  |
| --- | --- | --- |
| e 2017. Downloaded by Georgia Institute of Technology on 11/11/2017 03:33:50. | the strong ferroelectric properties in undoped 100–400 nm- | given in Fig. S6 in the ESI.† For this diagram, only the results |
| thick ZrO2 films when the films were prepared by a chemical solution deposition (CSD) method.26In their CSD films, | with identical ALD conditions (Hf[N(C2H5)CH3]4 (TEMA-Hf) as |
| the Hf precursor, Hf[N(C2H5)CH3]4 (TEMA-Zr) as the Zr-precur- |
| however, the Pr value in the pristine state was low and repeti- | sor, O3 as the oxygen source, an ALD temperature of 280 °C, |
| tive wake-up field cycling was required to achieve a feasible fer- | and TiN as the bottom electrode) and annealing conditions |
| roelectric performance.26This trend is different from that in | (500 °C for 30 seconds under a N2 atmosphere) were adopted |
| the report by Fan et al., suggesting that the o-phase formation | for consistency. The dielectric behaviour varies remarkably |
| in ZrO2 thin films remains unexplained.25From a thermo- | from an almost pure linear dielectric to a ferroelectric and an |
| dynamic point of view, a temperature much lower than room | antiferroelectric-like one. As seen in the figure, strong ferro- |
| temperature is required for the emergence of ferroelectricity in | electric properties could be achieved for the Zr/(Zr + Hf) ratio |
| ZrO2 thin films, in which a certain crystallite radius range | of roughly 0.4–0.6, and a thickness range of 5 to 20 nm. The |
| exists for the o-phase formation. However, none of the | t-phase region mostly coincides with the emergence of anti- |
| reported ferroelectric properties are at such low temperatures. | ferroelectric-like behaviour, and as can be readily anticipated, |
| Therefore, certain other mechanisms must be invoked to | the m-phase region coincides with the dielectric behaviour. At |
| explain the experimental observation of the ferroelectricity in | the phase boundary of the t- and o-phase, a broken hysteresis, |
| undoped ZrO2. Considering the fact that the ZrO2 film is prone | which is expected for a material with first order phase tran- |
| to in situ crystallization during film growth, the stress effect | sition slightly above Tc, could be observed.69Locally different |
| along a certain crystallographic direction may create a favour- | internal bias fields were also suggested to be the origin of |
| able environment for the o-phase formation. Further studies | pinched hysteresis in previous studies.70,71However, from the |
| are definitely needed to resolve this issue. | temperature-dependent P–E measurement in the previous |
| study, the broken hysteresis in HZO films is believed to be a |
| sign of a first order phase transition being the main cause of |
| the broken hysteresis in the samples used in this work.68Some |
| Published on 14 Jun |  | of the authors have claimed that such a broken hysteresis |
| properly arises at the morphotrophic phase boundary, and it |
| could be understood based on the classic first order phase |
| transition theory.68 |
| Even though the schematic diagram in Fig. 7 is expected to |
| provide a useful guideline for ALD of HZO films, it should be |
| noted that this schematic diagram has many limitations. It |
| cannot be applied to other deposition processes such as |
| chemical solution deposition,26physical vapour deposition,72 |
| metal–organic chemical vapour deposition,73,74pulsed laser |
| deposition, or even to atomic layer deposition with different |
| deposition conditions.19,75Even in the case of HZO films de- |
| posited using ALD, this schematic phase diagram is not quan- |
| titatively precise since the polymorphism in the HZO thin |
| films is affected by additional factors. Park et al. reported that |
| the annealing temperature could affect the experimental Pr |
| values, which should be strongly related to the o-phase frac- |
| tion.21,76According to previous studies, impurities such as |
| C,19N,18and H22are expected to influence the polymorphism |
| in doped HfO2 or HZO films. Moreover, the growth behaviour |
| and resulting polymorphism are also affected by the bottom |
| electrode materials.23,77All these process parameters may |

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Fig. 7 | Schematic | diagram | showing | the | dielectric | behaviour | of |

Hf1−xZrxO2 films deposited using atomic layer deposition for various film compositions and thicknesses (DE: dielectric, FE: ferroelectric, and AFE: antiferroelectric-like).

This journal is © The Royal Society of Chemistry 2017

influence the crystallite formation in the as-deposited state as well as after the crystallization annealing process. Although the electrical properties of ALD HZO films might be strongly affected by many additional factors, this schematic diagram is

Nanoscale, 2017, 9, 9973–9986 | 9983

**[View Article Online](http://dx.doi.org/10.1039/C7NR02121F)** Paper Nanoscale

believed to be a very useful qualitative guideline for the fabri-cation of HZO films with ferroelectric or antiferroelectric-like

capping layer were considered as well. Their effects seemed to have less influence in resolving the differences between theory

properties. and experiments. Finally, a schematic diagram of the dielectric

behaviours as a function of composition and thickness was

presented as a guideline for the fabrication of ferroelectric or

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Published on 14 June 2017. Downloaded by Georgia Institute of Technology on 11/11/2017 03:33:50. | Conclusion | antiferroelectric-like HZO films using the ALD process. | | | | | | |
| In conclusion, the crystallographic phases in ALD HZO films | Acknowledgements | | | | | | |
| were comprehensively studied by a comparison with the |
| thermodynamic surface energy model. The emergence of non- |
| stable or meta-stable o- and t-phases, which correspond to | C. S. H. acknowledges support from the Global Research | | | | | | |
| ferroelectric and antiferroelectric-like phases, respectively, in | Laboratory Program (2012K1A1A2040157) of the Ministry of | | | | | | |
| terms of the bulk free energy is due to the contribution of a | Science, ICT, and Future Planning and a grant from the | | | | | | |
| lower grain boundary or an interface energy of these meta- | National | | Research | Foundation | of | Korea | (NRF) |
| stable phases. A recent theoretical study of the surface energy | (no. | NRF-2014R1A2A1A10052979). | | | The | authors | acknow- |
| terms provided a solid support for such an assertion, but the | ledge | the | German | Research | Foundation | | (Deutsche |
| original report made the assumption that the grain boundary | Forschungsgemeinschaft) for funding part of this research in | | | | | | |
| and the interface energies are identical to the free surface energy, | the frame of the “Inferox” project (MI 1247/11-2). M. H. P. is | | | | | | |
| which is a problematic assumption. Therefore, a grain bound- | supported by a Humboldt postdoctoral fellowship from the | | | | | | |
| ary energy of 1/3 of the surface energy was assumed in this | Alexander von Humboldt Foundation. M. H. P. acknowledges | | | | | | |
| work. In addition, the distribution of the grain size in | the Basic Science Research Program through the National | | | | | | |
| annealed polycrystalline HZO films with different compo- | Research Foundation of Korea (NRF) funded by the Ministry of | | | | | | |
| sitions was also carefully and quantitatively included in the | Education (2016R1A6A3A03012208). The authors thank Bo- | | | | | | |
| theoretical estimation of the phase evolution based on the | Kyoung Kim from the RIAM at the SNU for the FE-SEM | | | | | | |
| total free energy, i.e. bulk energy and grain boundary energy, | analysis. | | | | | | |
| calculation. Although the overall trends, i.e. there are certain | References | | | | | | |
| composition and thickness ranges for the optimum ferroelec- |
| tric performances, of both the theoretical expectation and the |
| experimental results are consistent, there remains a critical |
| mismatch. The theory predicts that the optimum ferroelectric | 1 K. Ishikawa, K. Yoshikawa and N. Okada, Phys. Rev. B: | | | | | | |
| properties could be achieved near a Zr-concentration of about | Condens. Matter, 1988, 37, 5852–5855. | | | | | | |
| 70% and a film thickness of up to 25 nm. In contrast, the | 2 K. K. Nanda, A. Maisels, F. E. Kruis, H. Fissan and | | | | | | |
| experiment showed that a Zr-concentration of about 50% and | S. Stappert, Phys. Rev. Lett., 2003, 91, 106102. | | | | | | |
| a thin film thickness of less than 20 nm are the optimum con- | 3 F. D. Fischer, T. Waitz, D. Vollath and N. K. Simha, Prog. | | | | | | |
| ditions. Such a theoretical expectation can actually be applied | Mater. Sci., 2008, 53, 481–527. | | | | | | |
| to the case of a direct transition of a purely amorphous | 4 B. Medasani, Y. H. Park and I. Vasiliev, Phys. Rev. B: | | | | | | |

material into polycrystalline layers with specified grain size distributions. The experimental results are not necessarily reflecting this situation. In fact, the as-deposited ALD films have crystalline nuclei with a common size of 4 ± 0.5 nm, which was estimated using the Scherrer equation for the GIXRD peak broadening, for the films with Zr content from 47 to 100% having different degrees of crystallinity depending on

Condens. Matter, 2007, 75, 235436.

5 T. S. Böscke, J. Müller, D. Bräuhaus, U. Schröder and U. Böttger, Appl. Phys. Lett., 2011, 99, 102903.

6 X. Sang, E. D. Grimley, T. Schenk, U. Schröder and J. M. LeBeau, Appl. Phys. Lett., 2015, 106, 162905.

7 E. D. Grimley, T. Schenk, X. Sang, M. Pešić, U. Schroeder, T. Mikolajick and J. M. LeBeau, Adv. Electron. Mater., 2016,

the Zr-concentration. Higher Zr-concentration showed higher 2, 1600173.

degree of in situ crystallization. The theoretical calculations for 8 P. Polakowski and J. Müller, Appl. Phys. Lett., 2015, 106,

the stable phases of such small crystallites based on the 232905.

assumption that the interface energy between the crystallite 9 J. Müller, U. Schröder, T. S. Böscke, I. Müller, U. Böttger,

and the amorphous matrix is 1/3–1/2 of the free surface energy L. Wilde, J. Sundqvist, M. Lemberger, P. Kücher,

revealed that the o- and t-phases were stable at Zr-concen-trations of about 50% and about 70%, respectively. Therefore, these crystalline nuclei work as seeds for the heterogeneous

T. Mikolajick and L. Frey, J. Appl. Phys., 2011, 110, 114113. 10 S. Mueller, J. Mueller, A. Singh, S. Riedel, J. Sundqvist, U. Schroeder and T. Mikolajick, Adv. Funct. Mater., 2012,

nucleation and growth during the subsequent PMA process. 22, 2412–2417.

This interpretation matches very well with the observed electri-cal performance of the films with different compositions and thicknesses. The effect of the film stress (∼2 GPa) on the free energy of the crystalline phases and the role of the TiN

9984 | Nanoscale, 2017, 9, 9973–9986

11 S. Mueller, C. Adelmann, A. Singh, S. Van Elshocht, U. Schroeder and T. Mikolajick, Ferroelectricity in Gd-Doped HfO2 Thin Films, ECS J. Solid State Sci. Technol., 2012, 1, N123–N126.

This journal is © The Royal Society of Chemistry 2017

**[View Article Online](http://dx.doi.org/10.1039/C7NR02121F)**

Nanoscale Paper

12 T. Schenk, S. Mueller, U. Schroeder, R. Materlik, A. Kersch, 31 J. Müller, T. S. Böscke, U. Schröder, R. Hoffmann,

M. Popovici, C. Adelmann, S. Van Elshocht and T. Mikolajick and L. Frey, Electron Device Lett., 2012, 33,

T. Mikolajick, Strontium doped hafnium oxide thin films: 185–187.

Wide process window for ferroelectric memories, in 2013 Proceedings of the European Solid-State Device Research

32 S. Mueller, J. Muller, U. Schroeder and T. Mikolajick, IEEE Trans. Device Mater. Reliab., 2013, 99, 93–97.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Published on 14 June 2017. Downloaded by Georgia Institute of Technology on 11/11/2017 03:33:50. | Conference (ESSDERC), Bucharest, 2013, pp. 260–263, DOI: | | | | | | | | | | | | | | | | 33 M. | | Hoffmann, | | | M. | Pešić, | | K. | | Chatterjee, | | | | A. | | I. | | Khan, | |
| 10.1109/ESSDERC.2013.6818868. | | | | | | | | | | | | | | | | S. | Salahuddin, | | | | | S. | Slesazeck, | | | | U. | Schroeder | | | | | | | and |
| 13 J. Müller, T. S. Böscke, Y. Yurchuk, P. Polakowski, J. Paul, | | | | | | | | | | | | | | | | T. Mikolajick, Adv. Funct. Mater., 2016, 26, 8643–8649. | | | | | | | | | | | | | | | | | | | |
| D. Martin, T. Schenk, K. Khullar, A. Kersch, W. Weinreich, | | | | | | | | | | | | | | | | 34 M. H. Park, H. J. Kim, Y. J. Kim, T. Moon, K. D. Kim and | | | | | | | | | | | | | | | | | | | |
| S. Riedel, K. Seidel, A. Kumar, T. M. Arruda, S. V. Kalinin, | | | | | | | | | | | | | | | | C. S. Hwang, Adv. Energy Mater., 2014, 4, 1400610. | | | | | | | | | | | | | | | | | | | |
| T. Schlosser, R. Boschke, R. van Bentum, U. Schröder and | | | | | | | | | | | | | | | | 35 M. H. Park, H. J. Kim, Y. J. Kim, T. Moon, K. D. Kim and | | | | | | | | | | | | | | | | | | | |
| T. Mikolajick, IEEE Int. Electron Devices Meet., 2013, 10.8.1– | | | | | | | | | | | | | | | | C. S. Hwang, Nano Energy, 2015, 12, 131–140. | | | | | | | | | | | | | | | | | | | |
| 10.8.4, DOI: 10.1109/IEDM.2013.6724605. | | | | | | | | | | | | | | | | 36 M. Hoffmann, U. Schroeder, C. Künneth, A. Kersch, | | | | | | | | | | | | | | | | | | | |
| 14 U. Schroeder, S. Mueller, J. Mueller, E. Yurchuk, D. Martin, | | | | | | | | | | | | | | | | S. Starschich, U. Böttger and T. Mikolajick, Nano Energy, | | | | | | | | | | | | | | | | | | | |
| C. | Adelmann, | | | T. | Schloesser, | | | R. | van | | | Bentum | | | and | 2015, 18, 154–164. | | | | | | | | | | | | | | | | | | | |
| T. Mikolajick, Jpn. J. Appl. Phys., 2013, 2, N69–N72. | | | | | | | | | | | | | | | | 37 M. | | H. | Park, | T. | | Schenk, | | | M. | Hoffmann, | | | | | S. | | Knebel, | | |
| 15 S. Starschich, D. Griesche, T. Schneller and U. Böttger, ECS | | | | | | | | | | | | | | | | J. Gaertner, T. Mikolajick and U. Schroeder, Nano Energy, | | | | | | | | | | | | | | | | | | | |
| J. Solid State Sci. Technol., 2015, 4, P419–P423. | | | | | | | | | | | | | | | | 2017, 36, 381–389. | | | | | | | | | | | | | | | | | | | |
| 16 S. Starschich and U. Boettger, J. Mater. Chem. C, 2017, 5, | | | | | | | | | | | | | | | | 38 M. H. Park, H. J. Kim, Y. J. Kim, K. D. Kim, Y. H. Lee, | | | | | | | | | | | | | | | | | | | |
| 333–338. | | | | | | | | | | | | | | | | S. D. Hyun and C. S. Hwang, Adv. Mater., 2016, 28, 7956– | | | | | | | | | | | | | | | | | | | |
| 17 L. Xu, T. Nishimura, S. Shibayama, T. Yajima, S. Migita and | | | | | | | | | | | | | | | | 7961. | | | | | | | | | | | | | | | | | | | |
| A. Toriumi, Appl. Phys. Express, 2016, 9, 091501. | | | | | | | | | | | | | | | | 39 M. Pešić, M. Hoffmann, C. Richter, T. Mikolajick and | | | | | | | | | | | | | | | | | | | |
| 18 A. | G. | Chernikova, | | | D. | S. | Kuzmichev, | | | | D. | | V. | Negrov, | | U. Schroeder, Adv. Funct. Mater., 2016, 26, 7486–7494. | | | | | | | | | | | | | | | | | | | |
| M. G. Kozodaev, S. N. Polyakov and A. M. Markeev, Appl. | | | | | | | | | | | | | | | | 40 O. | Ohtaka, | | | H. | | fukui, | | T. | | Kunisada, | | | T. | | Fujisawa, | | | | |
| Phys. Lett., 2016, 108, 242905. | | | | | | | | | | | | | | | | K. Funakoshi, W. Utsumi, T. Irifune, K. Kuroda and | | | | | | | | | | | | | | | | | | | |
| 19 K. D. Kim, M. H. Park, H. J. Kim, Y. J. Kim, T. Moon, | | | | | | | | | | | | | | | | T. Kikegawa, J. Am. Ceram. Soc., 2001, 84, 1369–1373. | | | | | | | | | | | | | | | | | | | |
| Y. H. Lee, S. D. Hyun, T. Gwon and C. S. Hwang, | | | | | | | | | | | | | | | | 41 O. | Ohtaka, | | | H. | | fukui, | | T. | | Kunisada, | | | T. | | Fujisawa, | | | | |
| Ferroelectricity in undoped-HfO2 thin films induced by | | | | | | | | | | | | | | | | K. Funakoshi, W. Utsumi, T. Irifune, K. Kuroda and | | | | | | | | | | | | | | | | | | | |
| deposition temperature control during atomic layer depo- | | | | | | | | | | | | | | | | T. Kikegawa, Phys. Rev. B: Condens. Matter, 2001, 63, | | | | | | | | | | | | | | | | | | | |
| sition, J. Mater. Chem. C, 2016, 4, 6864–6872. | | | | | | | | | | | | | | | | 174108. | | | | | | | | | | | | | | | | | | | |
| 20 J. Müller, T. S. Böscke, U. Schröder, S. Müller, D. Bräuhaus, | | | | | | | | | | | | | | | | 42 R. Materlik, C. Künneth and A. Kersch, J. Appl. Phys., 2015, | | | | | | | | | | | | | | | | | | | |
| U. Böttger, L. Frey and T. Mikolajick, Nano Lett., 2012, 12, | | | | | | | | | | | | | | | | 117, 134109. | | | | | | | | | | | | | | | | | | | |
| 4318–4323. | | | | | | | | | | | | | | | | 43 R. C. Garvie, J. Phys. Chem., 1965, 69, 1238–1243. | | | | | | | | | | | | | | | | | | | |
| 21 M. H. Park, H. J. Kim, Y. J. Kim, W. Lee, T. Moon and | | | | | | | | | | | | | | | | 44 R. C. Garvie, J. Phys. Chem., 1978, 82, 218–224. | | | | | | | | | | | | | | | | | | | |
| C. S. Hwang, Appl. Phys. Lett., 2013, 102, 242905. | | | | | | | | | | | | | | | | 45 M. W. Pitcher, S. V. Ushakov, A. Navrotsky, B. F. Woodfield, | | | | | | | | | | | | | | | | | | | |
| 22 M. H. Park, H. J. Kim, Y. J. Kim, W. Lee, H. K. Kim and | | | | | | | | | | | | | | | | G. Li and J. Boerio-Goates, J. Am. Ceram. Soc., 2005, 88, | | | | | | | | | | | | | | | | | | | |
| C. S. Hwang, Appl. Phys. Lett., 2013, 102, 112914. | | | | | | | | | | | | | | | | 160–167. | | | | | | | | | | | | | | | | | | | |
| 23 M. H. Park, H. J. Kim, Y. J. Kim, T. Moon and C. S. Hwang, | | | | | | | | | | | | | | | | 46 M. Shandalov and P. C. Mclntyre, J. Appl. Phys., 2009, 106, | | | | | | | | | | | | | | | | | | | |
| Appl. Phys. Lett., 2014, 104, 072901. | | | | | | | | | | | | | | | | 084322. | | | | | | | | | | | | | | | | | | | |
| 24 S. | Zarubin, | | E. | Suvorova, | | | M. | Spiridonov, | | | | | D. | Negrov, | | 47 L. Vitos, A. V. Ruban, H. L. Skriver and J. Kollár, Surf. Sci., | | | | | | | | | | | | | | | | | | | |
| A. Chernikova, A. Markeev and A. Zenkevich, Appl. Phys. | | | | | | | | | | | | | | | | 1998, 411, 186–202. | | | | | | | | | | | | | | | | | | | |
| Lett., 2016, 109, 192903. | | | | | | | | | | | | | | | | 48 N. D. Lang and W. Kohn, Phys. Rev. B: Solid State, 1970, 1, | | | | | | | | | | | | | | | | | | | |
| 25 Z. Fan, J. Deng, J. Wang, Z. Liu, P. Yang, J. Xiao, X. Yan, | | | | | | | | | | | | | | | | 4555–4568. | | | | | | | | | | | | | | | | | | | |
| Z. Dong, J. Wang and J. Chen, Appl. Phys. Lett., 2016, 108, | | | | | | | | | | | | | | | | 49 A. B. Mukhopadhyay, J. F. Sanz and C. B. Musgrave, Phys. | | | | | | | | | | | | | | | | | | | |
| 012906. | | | | | | | | | | | | | | | | Rev. B: Condens. Matter, 2006, 73, 115330. | | | | | | | | | | | | | | | | | | | |
| 26 S. Starschich, T. Schenk, U. Schroeder and U. Boettger, | | | | | | | | | | | | | | | | 50 M. H. Park, Novel material and device for ferroelectric | | | | | | | | | | | | | | | | | | | |
| Appl. Phys. Lett., 2017, 110, 182905. | | | | | | | | | | | | | | | | memory: thin Hf1−xZrxO2 film and tri-states memory, PhD | | | | | | | | | | | | | | | | | | | |
| 27 M. | H. | Park, | | Y. | H. | Lee, | H. | J. | | Kim, | | Y. | | J. | Kim, | thesis, | | | Seoul | National | | | University, | | | | Republic | | | | of | | Korea, | | |
| T. Moon, K. D. Kim, J. Müller, A. Kersch, U. Schröder, | | | | | | | | | | | | | | | | 2014. | | | | | | | | | | | | | | | | | | | |
| T. Mikolajick and C. S. Hwang, Adv. Mater., 2015, 27, 1811– | | | | | | | | | | | | | | | | 51 D. Nečas and P. Klapetek, Cent. Eur. J. Phys., 2012, 10, 181– | | | | | | | | | | | | | | | | | | | |
| 1831. | | | | | | | | | | | | | | | | 188. | | | | | | | | | | | | | | | | | | | |

28 E. H. Kisi, J. Am. Ceram. Soc., 1998, 81, 741–745. 29 A. Navrotsky, J. Mater. Chem., 2005, 15, 1883–1890.

52 H. J. Kim, M. H. Park, Y. J. Kim, Y. H. Lee, T. Moon, K. D. Kim, S. D. Hyun and C. S. Hwang, Nanoscale, 2016, 8,

30 M. W. Pitcher, S. V. Ushakov, A. Navrotsky, B. F. Woodfield, 1383–1389.

G. Li, J. Boerio-Goates and B. M. Tissue, J. Am. Ceram. Soc., 53 D. M. Hausmann and R. G. Gordon, J. Cryst. Growth, 2003,

2005, 88, 160–167. 249, 251–261.

This journal is © The Royal Society of Chemistry 2017

Nanoscale, 2017, 9, 9973–9986 | 9985

**[View Article Online](http://dx.doi.org/10.1039/C7NR02121F)** Paper Nanoscale

54 T. Schenk, Formation of Ferroelectricity in Hafnium Oxide Based Thin Films, PhD thesis, TU Dresden, 2016.

55 J. W. Martin, R. D. Doherty and B. Cantor, Stability of Microstructure in Metallic Systems, Cambridge University

67 B.-T. Lin, Y.-W. Lu, J. Shieh and M.-J. Chen, J. Eur. Ceram. Soc., 2017, 37, 1135–1139.

68 M. H. Park, H. J. Kim, Y. J. Kim, Y. H. Lee, T. Moon, K. D. Kim, S. D. Hyun and C. S. Hwang, Appl. Phys. Lett.,

Press, UK, 1997. 2015, 107, 192907.

56 T. Shiraishi, K. Katayama, T. Yokouchi, T. Shimizu, T. Oikawa, O. Sakata, H. Uchida, Y. Imai, T. Kiguchi, T. J. Konno and

69 M. H. Park, H. J. Kim, Y. H. Lee, Y. J. Kim, T. Moon, K. D. Kim, S. D. Hyun and C. S. Hwang, Nanoscale, 2016, 8,

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Published on 14 June 2017. Downloaded by Georgia Institute of Technology on 11/11/2017 03:33:50. | H. Funakubo, Appl. Phys. Lett., 2016, 108, 26904. | | | | | | | | | | 13898–13907. | | | | | | | | | | |
| 57 K. | Tapily, | J. | E. | Jakes, | D. | Gu, | H. | Baumgart | and | 70 T. Schenk, M. Hoffmann, J. Ocker, M. Pešić, T. Mikolajick | | | | | | | | | | |
| A. A. Elmustafa, Int. J. Surf. Sci. Eng., 2011, 5, 193–204. | | | | | | | | | | and U. Schroeder, ACS Appl. Mater. Interfaces, 2015, 7, | | | | | | | | | | |
| 58 A. Toriumi, Y. Nakajima and K. Kita, ECS Trans., 2011, 41, | | | | | | | | | | 20224–20233. | | | | | | | | | | |
| 125–136. | | | | | | | | | | 71 F. P. G. Fengler, M. Pešić, S. Starschich, T. Schneller, | | | | | | | | | | |
| 59 H.-Y. Shih, W.-H. Lee, W.-C. Kao, Y.-C. Chuang, R.-M. Lin, | | | | | | | | | | C. Kuenneth, U. Bttger, H. Mulaosmanovic, T. Schenk, | | | | | | | | | | |
| H.-C. Lin, M. Shiojiri and M.-J. Chen, Sci. Rep., 2017, 7, | | | | | | | | | | M. H. Park, R. Nigon, P. Muralt, T. Mikolajick and | | | | | | | | | | |
| 39717. | | | | | | | | | | U. Schroeder, Adv. Electron. Mater., 2017, 3, 1600505. | | | | | | | | | | |
| 60 S. W. Lee, B. J. Choi, T. Eom, J. H. Han, S. K. Kim, | | | | | | | | | | 72 T. Kiguchi, S. Nakamura, A. Akama, T. Shiraishi and | | | | | | | | | | |
| S. J. Song, W. Lee and C. S. Hwang, Coord. Chem. Rev., | | | | | | | | | | T. J. Konno, J. Ceram. Soc. Jpn., 2016, 124, 689–693. | | | | | | | | | | |
| 2013, 257, 3154–3176. | | | | | | | | | | 73 T. | Shimizu, | | T. | Yokouchi, | | T. | Shiraishi, | | T. | Oikawa, |
| 61 A. L. Patterson, Phys. Rev., 1939, 56, 978–982. | | | | | | | | | | P. | S. | Sankara | | Rama | Krishnan | | and | H. | Funakubo, | |
| 62 F. Bohra, B. Jiang and J.-M. Zuo, Appl. Phys. Lett., 2007, 90, | | | | | | | | | | Jpn. J. Appl. Phys., 2014, 53, 09PA04. | | | | | | | | | | |
| 161917. | | | | | | | | | | 74 T. Shimizu, T. Yokouchi, T. Oikawa, T. Shiraishi, T. Kiguchi, | | | | | | | | | | |
| 63 M.-S. Kim, Y.-D. Ko, M. Yun, J.-H. Hong, M.-C. Jeong, | | | | | | | | | | A. Akama, T. J. Konno, A. Gruverman and H. Funakubo, | | | | | | | | | | |
| J.-M. Myoung and I. Yun, Mater. Sci. Eng., B, 2005, 123, 20–30. | | | | | | | | | | Appl. Phys. Lett., 2015, 106, 112904. | | | | | | | | | | |
| 64 S. V. Ushakov, A. Navrotsky, Y. Yang, S. Stemmer, K. Kukli, | | | | | | | | | | 75 A. Chernikova, M. Kozodaev, A. Markeev, D. Negrov, | | | | | | | | | | |
| M. Ritala, M. A. Leskelä, P. Fejes, A. Demkov, C. Wang, | | | | | | | | | | M. Spiridonov, S. Zarubin, O. Bak, P. Buragohain, H. Lu, | | | | | | | | | | |
| B.-Y. Nguyen, D. Triyoso and P. Tobin, Phys. Status Solidi B, | | | | | | | | | | E. Suvorova, A. Gruverman and A. Zenkevich, ACS Appl. | | | | | | | | | | |
| 2004, 241, 2268–2278. | | | | | | | | | | Mater. Interfaces, 2016, 8, 7232–7237. | | | | | | | | | | |
| 65 D. A. Porter, K. E. Easterling and M. Y. Sherif, Phase | | | | | | | | | | 76 M. H. Park, H. J. Kim, Y. J. Kim, T. Moon, K. D. Kim and | | | | | | | | | | |
| Transformations in Metals and Alloys, CRC Press, USA, 3rd | | | | | | | | | | C. S. Hwang, Phys. Status Solidi RRL, 2014, 8, 857–861. | | | | | | | | | | |
| edn, 2009. | | | | | | | | | | 77 M. H. Park, H. J. Kim, Y. J. Kim, W. Lee, T. Moon, | | | | | | | | | | |
| 66 A. Pal, V. K. Narasimhan, S. Weeks, K. Littau, D. Pramanik | | | | | | | | | | K. D. Kim and C. S. Hwang, Appl. Phys. Lett., 2014, 105, | | | | | | | | | | |
| and T. Chiang, Appl. Phys. Lett., 2017, 110, 022903. | | | | | | | | | | 072902. | | | | | | | | | | |

9986 | Nanoscale, 2017, 9, 9973–9986

This journal is © The Royal Society of Chemistry 2017