**The origin of ferroelectricity in Hf1-xZrxO2: A computational investigation and a surface energy model**   
[R. Materlik](http://aip.scitation.org/author/Materlik%2C+R), [C. Künneth](http://aip.scitation.org/author/K%C3%BCnneth%2C+C), and [A. Kersch](http://aip.scitation.org/author/Kersch%2C+A)

Citation: Journal of Applied Physics**117**, 134109 (2015); View online: <https://doi.org/10.1063/1.4916707>  
View Table of Contents: <http://aip.scitation.org/toc/jap/117/13>Published by the [American Institute of Physics](http://aip.scitation.org/publisher/)

**Articles you may be interested in**   
[Stabilizing the ferroelectric phase in doped hafnium oxide](http://aip.scitation.org/doi/abs/10.1063/1.4927805)   
[Journal of Applied Physics](http://aip.scitation.org/doi/abs/10.1063/1.4927805) **[118](http://aip.scitation.org/doi/abs/10.1063/1.4927805)**[, 072006 (2015); 10.1063/](http://aip.scitation.org/doi/abs/10.1063/1.4927805)1.4927805   
[Ferroelectricity in hafnium oxide thin films](http://aip.scitation.org/doi/abs/10.1063/1.3634052)   
[Applied Physics Letters](http://aip.scitation.org/doi/abs/10.1063/1.3634052) **[99](http://aip.scitation.org/doi/abs/10.1063/1.3634052)**[, 102903 (2011](http://aip.scitation.org/doi/abs/10.1063/1.3634052)); 10.1063/1.3634052   
[Evolution of phases and ferroelectric properties of thin Hf0.5Zr0.5O2 films according to the thickness and annealing temperature](http://aip.scitation.org/doi/abs/10.1063/1.4811483)   
[Applied Physics Letter](http://aip.scitation.org/doi/abs/10.1063/1.4811483)s **102**, 242905 (2013); 10.1063/1.4811483   
[On the structural origins of ferroelectricity in HfO2 thin films](http://aip.scitation.org/doi/abs/10.1063/1.4919135)   
Applied Physics Letters **106**, 162905 (2015); 10.1063/1.4919135   
[Ferroelectricity in undoped hafnium oxide](http://aip.scitation.org/doi/abs/10.1063/1.4922272)   
[Applied Physics Letters](http://aip.scitation.org/doi/abs/10.1063/1.4922272) **[106](http://aip.scitation.org/doi/abs/10.1063/1.4922272)**[, 232905 (201](http://aip.scitation.org/doi/abs/10.1063/1.4922272)5); 10.1063/1.4922272   
[Ferroelectricity in yttrium-doped hafnium oxide](http://aip.scitation.org/doi/abs/10.1063/1.3667205)   
[Journal of Applied Physics](http://aip.scitation.org/doi/abs/10.1063/1.3667205) **[110](http://aip.scitation.org/doi/abs/10.1063/1.3667205)**[, 114113 (2011)](http://aip.scitation.org/doi/abs/10.1063/1.3667205); 10.1063/1.3667205



JOURNAL OF APPLIED PHYSICS 117, 134109 (2015) 

[The origin of ferroelectricity in Hf1](http://dx.doi.org/10.1063/1.4916707)2[xZrxO2: A computational investigation and a surface energy model](http://dx.doi.org/10.1063/1.4916707)

R. Materlik, C. K€unneth, and A. Kerscha)   
Department of Applied Sciences and Mechatronics, Munich University of Applied Sciences, Lothstr. 34, 80335 Munich, Germany

(Received 1 February 2015; accepted 22 March 2015; published online 7 April 2015)

The structural, thermal, and dielectric properties of the ferroelectric phase of HfO2, ZrO2, and Hf0.5Zr0.5O2 (HZO) are investigated with carefully validated density functional computations. We find that the free bulk energy of the ferroelectric orthorhombic Pca21 phase is unfavorable compared to the monoclinic P21/c and the orthorhombic Pbca phase for all investigated stoichiometries in the Hf1�xZrxO2 system. To explain the existence of the ferroelectric phase in nanoscale thin films, we explore the Gibbs/Helmholtz free energies as a function of stress and film strain and find them

unlikely to become minimal in HZO films for technological relevant conditions. To assess the contribution of surface energy to the phase stability, we parameterize a model, interpolating

between existing data, and find the Helmholtz free energy of ferroelectric grains minimal for a range

of size and stoichiometry. From the model, we predict undoped HfO2 to be ferroelectric for a grain size of about 4 nm and epitaxial HZO below 5 nm. Furthermore, we calculate the strength of an

applied electric field necessary to cause the antiferroelectric phase transformation in ZrO2 from the P42/nmc phase as 1 MV/cm in agreement with experimental data, explaining the mechanism of field induced phase transformation. V C 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4916707>]

I. INTRODUCTION

The recent discovery of ferroelectricity in HfO2 and ZrO2 based high-k materials1,2surprised, since this material class was extensively studied for decades.3,4Similar to the classical perovskites, the origin of the ferroelectricity is most likely a non-centrosymmetric polar crystal phase which is stable under certain conditions. Kisi5found and structurally analyzed the polar orthorhombic Pca21 phase (f-phase) more than 2 decades ago in ZrO2 under asymmetric stress condi-tions. In this time, theoretical calculations were performed6 showing such a phase to be stable. Neither the dielectric properties were studied experimentally nor examined by calculations. The discovery of the ferroelectric properties arose from the development of nanoscale thin films7for use in memory technology, where crystalline doped films of high quality were developed. After the observation of a remanent polarization and hysteresis in 10 nm thick films of 3% Si doped HfO2 films1in a TiN-HfO2-TiN stack, the effect was additionally found in Al- and Y-doped films8,9grown on TiN as well. More suitable dopants have been discovered since.10 Furthermore, ferroelectricity was found in the 9 nm mixed oxide thin film Hf0.5Zr0.5O2 (HZO)2deposited on TiN elec-trodes, although neither the pure HfO2 nor the pure ZrO2 film exhibit ferroelectricity. The existence of a true ferro-electric effect has been confirmed by various experiments such as P-V and C-V measurements8as well as retention ex-trapolated up to 10 yr (Ref. 12) and the occurrence of ortho-rhombic peaks in XRD measurements.13ZrO2 was also studied extensively in the context of functional thin films, since its tetragonally stabilized form has a high dielectric

a)Author to whom correspondence should be addressed. Electronic mail: [akersch@hm.edu](mailto:akersch@hm.edu)

constant. M€uller11showed that ZrO2 behaves antiferroelec-

|  |
| --- |
| tric: above a critical field in the order of 1 MV/cm, a temper- |

|  |
| --- |
| ature dependent field induced phase transformation to the f- |

phase occurs. A recent review of the current status of HfO2, ZrO2, and HZO based ferroelectric films can be found in Ref. 10.

Although the ferroelectricity in binary oxides is similar to perovskites, there are some differences which make these materials highly attractive for technological applications: the binary oxides do not suffer from a dead layer effect which makes perovskites ineffective for thin film technology. The mid range dielectric constant8of the binary oxides allows switching at moderate voltage, although the necessary field strength required for polarization reversal is much higher than for perovskites.14The large field strength without

|  |
| --- |
| breakdown is possible due to the large band gap of 5.6 eV |

compared to 3–5 eV in perovskites.15   
 Despite intense research in the last years to collect phe-nomenological knowledge and explore the fundamental effects, an open issue remains which is of some relevance for

|  |
| --- |
| the fundamental understanding as well as for the technological |

|  |
| --- |
| applications: what is the exact reason for the stability of the |

|  |
| --- |
| ferroelectric phase in the various conditions where it has been |

found? As a fact, the bulk materials have not been stabilized in the ferroelectric f-phase so far, whereas the possible influ-encing factors on phase stability like temperature, doping and other defects, stress or strain, and surface or interface energy are known. It is under intensive investigation what specific set of circumstances is responsible for the existence of the experi-mental observed ferroelectric thin films.

The effect of doping to promote cubic Fm-3m (c-phase) or tetragonal P42/nmc (t-phase) phases is well known from partially and fully stabilized ceramics. The ferroelectric

|  |  |  |
| --- | --- | --- |
| 0021-8979/2015/117(13)/134109/15/$30.00 | 117, 134109-1 | V C 2015 AIP Publishing LLC |

|  |  |  |
| --- | --- | --- |
| 134109-2 | Materlik, K€unneth, and Kersch | J. Appl. Phys. 117, 134109 (2015) |

f-phase was originally discovered in Si doped HfO2.1So far all subsequently produced ferroelectric films were doped as well, with the exception of HZO films. However, to com-pletely explain f-phase stability, there is still a need for an additional mechanism since the ferroelectric properties typi-cally disappear in thick films and bulk materials.16In this pa-per, we want to focus on the binary mixed oxide Hf0.5Zr0.5O2 to minimize computational load otherwise necessary for cal-culations with dopants.

Since the discovery of transformation toughening by Garvie,17the importance of stress effects causing the transi-tion of stabilized tetragonal into the monoclinic P21/c phase (m-phase) is well known in ZrO2. Asymmetric stress effects have also been discussed as an explanation for the appear-ance of ferroelectric ZrO2 grains in cubic stabilized ZrO2.18 Furthermore, stress effects in thin Hf0.5Zr0.5O2 films have been used as a possible explanation of how a cap electrode affects the ferroelectric phase by M€uller11,19as well as film thickness causing film stress variation and appearance of a ferroelectric phase by Park.16   
 The effect of grain size on phase stability is well known from the work of Garvie17and has an important application in ZrO2 thin films contained in the high-k dielectric of DRAM capacitors. These ZrO2 films with grain size below 30 nm are typically in the t-phase and the involved surface energy relative to the m-phase was experimentally measured by Pitcher et al. and other groups20,21and calculated by Christensen and Carter.22The same effect is known for HfO2 which undergoes a phase transformation at a critical particle size of about 4 nm, but the surface energy has only been measured for the m-phase.23M€uller2observed the size effect in ferroelectric Hf0.5Zr0.5O2 thin films by identifying the

|  |
| --- |
| thinner 7.5 nm film as less ferroelectric and more antiferro- |

electric than the thicker 9 nm film. This investigation was deepened in the systematic work by Park24who found a loss of ferroelectricity for films above 20 nm.

In this paper, we investigate the stability of the f-phase with density functional calculations (DFT). Section II describes the computational setup. In Secs. III A–III C, the computed structures and total and free energies for various polymorphs are presented and compared with literature data. The phonon modes and the infrared (IR) spectra are com-

II. COMPUTATIONAL METHODS

All calculations are performed using the ABINIT pack-age.25,26The exchange-correlation energy is computed with a local-density approximation using the Perdew-Wang parameterization. For Hf, we use a self made norm-conserving Troullier-Martin pseudopotential generated with the fhi98 generator27to achieve good values for the lattice constants. For Zr and O, we use well calibrated RRKJ norm-conserving pseudopotentials from the Opium pro-ject.31The levels Hf(5s,5p,5d,6s), Zr(4s,4p,4d,5s), and O(2s,2p) are treated as valence states with the following atomic valence configurations for the reference state: Hf(5s25p65d26s2), Zr(4s24p64d05s0), and O(2s22p4). For Hf, core radii of 1.3 a0, 1.8 a0, and 2.7 a0 (Bohr radii) are cho-sen to describe angular waves from s to d. For Zr, the cutoff radii were 1.58 a0, 1.73 a0, and 1.79 a0 whereas for the O pseudopotential, a cutoff radius of 1.50 a0 for both s and p waves is applied. We also adopted a separable form for the pseudopotentials treating the following angular momentum waves as local: s for Hf, f for Zr, and p for O. For Hf, a non-linear core correction of radius 1.05 a0 was used.28   
 The Brillouin zone is sampled using the Monkhorst-Pack29scheme with a 6 � 6 � 6 k-point grid for all 12 atomic phases and a 3 � 6 � 6 for the 24 atomic orthorhombic Pbca phase (o-phase). The cutoff energy Ecut of the plane-wave expansion was fixed at 30 Ha. For the calculation of the pho-non modes, a 2 � 2 � 2 q-point grid was calculated and inter-polated to a 30 � 30 � 30 grid.30Integration of the phonon density of states yields the free energy. All parameters were carefully tested for convergence. The acoustic sum rule was imposed.

HZO cells are constructed by replacing 50% of Zr atoms in ZrO2 with Hf. There are two inequivalent possibilities to build such a cell, but the difference in total energy and other properties between both is negligible small. To save CPU time, we choose one (see SI,32Table SI) for our calculations.

Berry phase calculations were performed under an incre-mentally increasing electric field to study the effect of an external electrical field on m-, t-, and f-phase cells. Structural relaxations are performed after each increase of 1 MV/cm in electric field strength.

puted as well. Since absolute values for total energies in III. RESULTS

DFT calculations are known to depend on the exchange-correlation functional and pseudopotential on the level of a few meV/f.u. (f.u. ¼ formula unit MO2, M ¼ Hf, Zr), we val-idate our choice by comparison with available data. In Subsection III D, the effects of stress and strain together with elastic properties are included, and possible scenarios for a stress or strain stabilization are discussed. In Subsection III E, the effects of surface energy are included in the form of a model. The model contains free parameters in the form of surface energies based on the limited amount of experi-mental and calculated data available so far. The results are discussed in light of a variety of experimental results. Subsection III F contains the computed effect of an electric field on the phase stability as well as the dielectric and ferro-electric properties. The conclusions are presented in Sec. IV.

A. Structural properties

HfO2 and ZrO2 are structurally and chemically similar33 and can adopt a variety of crystalline phases. Increasing the temperature, the monoclinic phase (m-phase, No. 14, space group (SG): P21/c) transforms (between 1270 K and 1370 K for ZrO2 3 and at about 2073 K for HfO2 3,34) into a tetragonal phase (t-phase, No. 137, SG: P42/nmc) and further (at about 2650 K for ZrO2 3 and about 2900 K for HfO2 3) into a cubic phase (c-phase, No. 225, SG: Fm3m). In addition, various orthorhombic phases exist: an orthorhombic I phase (o-phase, No. 61, SG: Pbca), an orthorhombic II phase (oII-phase, No. 62, SG: Pnma), and a polar orthorhombic III phase (f-phase, No. 29, SG: Pca21). The phase transformation from the m- to the o-phase can be observed at a compressive pressure of

|  |  |  |
| --- | --- | --- |
| 134109-3 | Materlik, K€unneth, and Kersch | J. Appl. Phys. 117, 134109 (2015) |

TABLE I. Calculated lattice constants a, b, and c41for a unit cell in A˚. a0, b0, and c0are the lattice constants of a 12 atomic cell with less than 12 atoms per unit cell. The cell volume V is in A˚ 3, and the total energy difference DU in meV/f.u. The lattice constants are aligned with the direction x, y, z, and z\* (given in Miller vector notation) as defined in Fig. 1. b is the angle of the m-phase between x and z\*. The Wyckoff positions of the metals (M) and oxygen atoms (O1 and O2) are given in relative coordinates. The arrows indicate the polarization direction of the f-phase.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  |  | c-ZrO2 |  |  | c-HfO2 |  |
| M b | x ¼ [100] a0¼ 5.05 | DU ¼ 96 V ¼ 129.2 | z ¼ [001]  c0¼ 5.05 | x ¼ [100] a0¼ 5.04 | DU ¼ 112 V ¼ 128.4 | z ¼ [001] c0¼ 5.04 |
| y ¼ [010]  b0¼ 5.05 | y ¼ [010]  b0¼ 5.04 |
| 0.250 | 0.000 | 0.250 | 0.250 | 0.000 | 0.250 |
| O1 c | 0.000 | 0.250 | 0.000 | 0.000 | 0.250 | 0.000 |
| O2 c | 0.500 | 0.250 | 0.500 | 0.500 | 0.250 | 0.500 |
| t-ZrO2 | t-HfO2 |
|  |  | DU ¼ 49 V ¼ 131.8 |  |  | DU ¼ 92 V ¼ 131.1 |  |
|  | x ¼ [110] a0¼ 5.06 | y ¼ [001]  c ¼ 5.15 | z ¼ [110]  b0¼ 5.06 | x ¼ [110] a0¼ 5.05 | y ¼ [001]  c ¼ 5.14 | z ¼ [110] b0¼ 5.05 |
| M b | 0.250 | 0.000 | 0.250 | 0.250 | 0.000 | 0.250 |
| O1 d | 0.000 | 0.294 | 0.000 | 0.000 | 0.293 | 0.000 |
| O2 d | 0.500 | 0.206 | 0.500 | 0.500 | 0.207 | 0.500 |
| m-ZrO2 | m-HfO2 |
|  |  | DU ¼ 0 V ¼ 138.5 b ¼ 80.5� |  |  | DU ¼ 0 V ¼ 138.4 b ¼ 80.3� |  |
|  | x ¼ [100] a ¼ 5.11 | y ¼ [010]  b ¼ 5.22 | z\* ¼ [001]  c ¼ 5.27 | x ¼ [100] a ¼ 5.12 | y ¼ [010]  b ¼ 5.18 | z\* ¼ [001] c ¼ 5.29 |
| M 4e | 0.278 | 0.043 | 0.290 | 0.276 | 0.042 | 0.292 |
| O1 4e | 0.074 | 0.334 | 0.165 | 0.068 | 0.331 | 0.153 |
| O2 4e | 0.553 | 0.258 | 0.481 | 0.550 | 0.257 | 0.480 |

f-ZrO2 #   
DU ¼ 37 V ¼ 133.8

f-HfO2 #   
DU ¼ 62 V ¼ 133.5

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | x ¼ [010]  b ¼ 5.04 | y ¼ [100]  a ¼ 5.25 | z ¼ [001]  c ¼ 5.06 | x ¼ [010]  b ¼ 5.04 | y ¼ [100]  a ¼ 5.23 | z ¼ [001] c ¼ 5.06 |
| M 4a | 0.268 | 0.032 | 1=4 þ 0.002  1=4�0.133  1=2þ0.006 | 0.267 | 0.032 | 1=4 þ 0.007 1=4�0.138 1=2þ0.008 |
| O1 4a | 0.073 | 0.369 | 0.068 | 0.389 |
| O2 4a | 0.539 | 0.266 | 0.537 | 0.267 |

f-ZrO2 "   
DU ¼ 37 V ¼ 133.8

f-HfO2 "   
DU ¼ 62 V ¼ 133.5

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | x ¼ [010] b ¼ 5.04 | y ¼ [100]  a ¼ 5.25 | z ¼ [001] c ¼ 5.06 | x ¼ [010]  a ¼ 5.04 | y ¼ [100]  b ¼ 5.23 | z ¼ [001] c ¼ 5.06 |
| M 4a | 0.268 | 0.032 | 1=4 � 0.002 1=4þ0.133 1=2�0.006 | 0.267 | 0.032 | 1=4 � 0.007 1=4þ0.138 1=2�0.008 |
| O1 4a | 0.073 | 0.369 | 0.068 | 0.389 |
| O2 4a | 0.539 | 0.266 | 0.537 | 0.267 |
| o-ZrO2 | o-HfO2 |
|  |  | DU ¼ 26 V ¼ 138.7 |  |  | DU ¼ 24 V ¼ 138.4 |  |
|  | x ¼ [100] a/2 ¼ 5.07 | y ¼ [010]  b ¼ 5.20 | z ¼ [001] c ¼ 5.27 | x ¼ [100]  a/2 ¼ 5.07 | y ¼ [010]  b ¼ 5.15 | z ¼ [001] c ¼ 5.29 |
| M 8c | 0.278/2 | 0.042 | 0.340 | 0.276/2 | 0.041 | 0.343 |
| O1 8c | 0.069/2 | 0.338 | 0.174 | 0.064/2 | 0.325 | 0.160 |
| O2 8c | 0.552/2 | 0.249 | 0.589 | 0.550/2 | 0.248 | 0.589 |

|  |  |  |
| --- | --- | --- |
| 134109-4 | Materlik, K€unneth, and Kersch | J. Appl. Phys. 117, 134109 (2015) |

about 4–12 GPa in bulk for HfO2 35,36 and ZrO2.37,38 The oII-

phase occurs at a very high compressive pressure above

20 GPa for both HfO2 36 and ZrO2.38 We do not include this

high pressure phase in our study, since such high pressures

are irrelevant for most thin film applications. The transforma-

tion to the polar f-phase can be observed under asymmetric

stress conditions18which will be discussed in Sec. III C.

Although the unit cell of the c-phase has only 3 and the

particular chiral form as both structures have the same total energies and hence decided for the mirror reflected structure shown in Fig. 1 based upon better visualization of the polar-ization reversal. Furthermore, the 24 atomic unit cell of the o-phase can be constructed by gluing the two illustrated unit cells of the f-phase with opposite polarization and chirality alongside the xy-plane together and relaxing the structure. Therefore, the o-phase has one additional symmetry com-

t-phase only 6 atoms, we represent all the structures except pared to the f-phase.

the o-phase in 12 atom cells for a better visualization of the structural similarity. The Wyckoff coordinates are shown in Table I and the structures in Fig. 1.39The polarization of the f-phase can be visualized in the form of the displacement of the four O1 atoms in the z-direction after polarization reversal by mirror reflection, whereas the metal and O2 atoms are hardly displaced. When the motion of an atom i in direction j is Drij relative to the mirror symmetric, polarization neutral configuration, the polarization Pj of the structure is

The similarity between structures can be better under-stood by comparing the relative coordinates of the Wyckoff positions in an appropriate representation (choice of origin). The chosen representation allows the construction of an ini-tial reaction path for the calculation of the phase transforma-

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| tion | to | determine | the | transition | state. | The | relative |

coordinates and cell parameters of the calculated structures are shown in Table I. The representations of the structures were checked with FINDSYM.40   
 A martensitic phase transformation between crystal

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Pj ¼e V� | X | Z � Dr; | (1) | structures requires a specific spatial orientation due to con- |
| X | Z ij�rij |  | straints by transition path and barrier. The orientation |
| between the t- and m-phase during temperature driven-phase |

with cell volume V, Born charge tensor Z\*ij, and unit charge e. Upon a point reflection, the polarization changes as well, but the resulting structure is unequal to the mirror reflected structure. The reason is that the f-phase appears to occur in two different forms with opposite chirality. We are unaware of any physical reason to discriminate in favor of any

transformations has been investigated experimentally and theoretically.42,43It was found that the [010]m jj [001]t direc-tions and the (100)m jj (110)t planes coincide. In addition, the spatial orientation between the t- and f-phase has been investigated by Kisi4who found a similar coincidence of

[010]f jj [001]t and (100)f jj (110)t. The spatial orientation

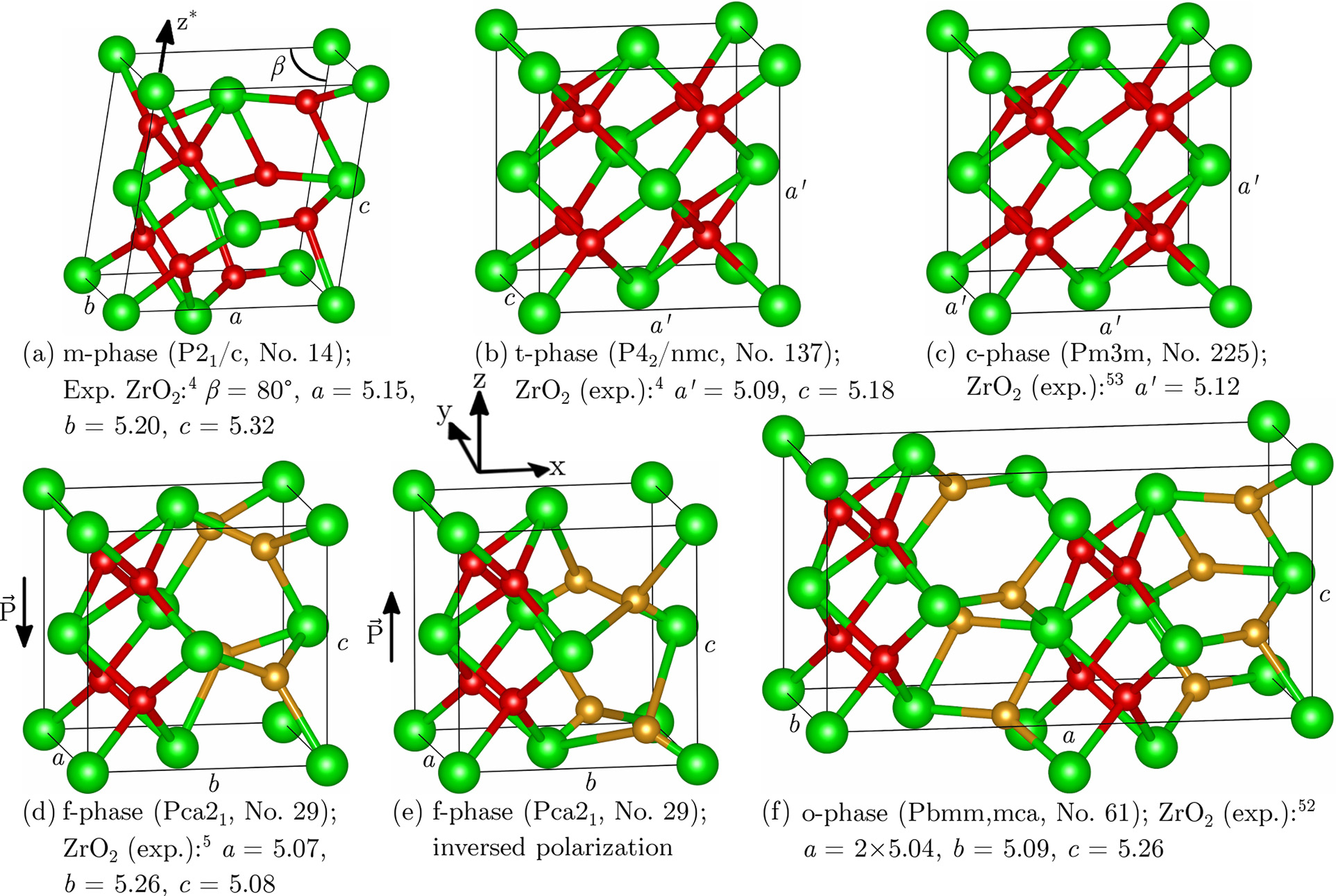


FIG. 1. Crystal phases39and experimental lattice constants in A˚ for ZrO2. Zr atoms are represented in green (big) and O atoms in red (small). In the f-phases, the O atoms mainly responsible for the polarization are highlighted golden. To illustrate the relationship between the f- and o-phases, the corresponding O atoms are highlighted in the o-phase as well. The polarization axis of the two f-phase cells is marked by black arrows (P).

|  |  |  |  |
| --- | --- | --- | --- |
| 134109-5 | Materlik, K€unneth, and Kersch | B. Total energy | J. Appl. Phys. 117, 134109 (2015) |
| between the f- and o-phase is derived from the representation | |

in Fig. 1 and implies a spatial relation between the o- and m-phase via the f- and t-phase.

In the following discussion, we will focus on ZrO2 to further exemplify the relation between the various phases (values from Table I). The m ! t transition involves a vol-ume change from 138.5 A˚ 3to 131.8 A˚ 3and the change of c from 5.27 A˚ to 5.06 A˚ . Besides the difference of the lattice angle b, the main distinction between the m- and the f-phase is a polarization dependent displacement of the O1 atom in z-direction. The o-phase is closely related to the f-phase because the 24 atomic cell is composed of two oppositely polarized 12 atomic f-phase cells. Nonetheless, the cell vol-ume and lattice constants differ: the volume changes from 138.7 A˚ 3to 133.8 A˚ 3and the length of the polarization axis c from 5.27 A˚ to 5.06 A˚ . The experimental results show only a small difference in volume and length between these two phases. A transformation from the m-phase to the f-phase involves a volume change from 138.5 A˚ 3to 133.8 A˚ 3and a reduced length of the polarization direction c from 5.27 A˚ to 5.06 A˚ . The transformation from the t-phase to the f-phase involves only a volume change from 131.8 A˚ 3to 133.8 A˚ 3

The structural relaxation provides values for the specific total energy per f.u. for each phase. Table I contains the cal-culated total energy differences DU relative to the m-phase. These values constitute the foundation of the calculation of the phase stability, since the relevant criteria like the Helmholtz free energy and the Gibbs energy are calculated from this difference by adding a temperature or pressure

TABLE II. Comparison of lattice constants a, b, and c in A˚ and total energy difference DU in meV/f.u. for HfO2. Bold values highlight experimental results.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Structure | DUa(meV) | V (A˚ 3) | Axz (A˚ 2) | a (A˚ ) | b (A˚ ) | c (A˚ ) | Method |
| reference |
| m-HfO2 | / | 137.9 | 26.7 | 5.12 | 5.17 | 5.29 | Exp.45 |
| / | 135.8 | 26.4 | 5.07 | 5.14 | 5.29 | Exp.11 |
| 0 | 137.1 | 26.6 | 5.11 | 5.16 | 5.28 | LDAb |
| 0 | 136.1 | 26.4 | 5.09 | 5.16 | 5.26 | LDA46 |
| 0 | 125.3 | 24.8 | 4.95 | 5.06 | 5.08 | LDA47 |
| 0 | 130.9 | … | … | … | … | LDA48 |
| 0 | 139.0 | 26.8 | 5.13 | 5.19 | 5.30 | GGA48 |
| 0 | 139.8 | 26.9 | 5.14 | 5.20 | 5.31 | GGA49 |

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| and the polarization direction c has almost no change. At this | 0 | 138.2 | 26.6 | 5.12 | 5.19 | 5.28 | PAW46 |

point, a transformation to the f-phase seems to be easiest from the t-phase although both phases have no close symme-

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| DUa | V | Axz | a0 | c0 | b0 |

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| try relationship. Comparing Hf and Zr, all the HfO2 cells are | c t-HfO2 | / | 133.1 | 25.6 | 5.06 | 5.20 | . . . | Exp.45 |
| slightly smaller than the ZrO2 cells consistent with the lan-thanide contraction argument.33 | / | 133.1 | 25.6 | 5.06 | 5.20 | . . . | Exp.50 |
| 92 | 129.5 | 25.3 | 5.03 | 5.12 | … | LDAb |
| 71 | 118.8 | 24.0 | 4.90 | 4.95 | … | LDA47 |
| It is known that the accuracy of the calculated results |
| >60 | 135.2 | 25.6 | 5.06 | 5.28 | … | LDA49 |
| depend on the chosen density functional and pseudo- |
| 99 | 125.1 | … | … | … | … | LDA48 |
| potential. While lattice constants from generalized gradient |
| 156 | 133.1 | 25.6 | 5.06 | 5.20 | … | GGA48 |
| approximation (GGA) calculations are typically too large, |
| 138 | 130.3 | 25.3 | 5.03 | 5.15 | … | PAW46 |
| the results from local density approximation (LDA) calcula- |
| DUa | V | Axz | b | a | c |
| tions are typically too small (about 1%). However, the dis- |
| crepancy for the LDA decreases, when the expansion effect | f-HfO2 | / | … | … | … | … | … | Exp. |
| of zero point motion is included.44Furthermore, the calcu- |
| 62 | 132.1 | 25.3 | 5.02 | 5.22 | 5.04 | LDAb |
| lated results depend on the chosen basis set and the number | 48 | 121.0 | 23.9 | 4.88 | 5.07 | 4.89 | LDA47 |
| of k-points which were not always well documented in the | 24 | 138.1 | 26.1 | 5.10 | 5.30 | 5.11 | LDA6 |
| previous studies. In Tables II, III, and IV, we compare our | >30 | 134.6 | 25.5 | 5.01 | 5.29 | 5.08 | GGA49 |
| 63 | 102.8 | 24.1 | 4.90 | 5.11 | 4.92 | PAW46 |
| calculated results for lattice constants of HfO2, HZO, and |

ZrO2, respectively, with calculated values and with experi-mental data found in literature about the investigated phases. For HZO, only our own calculated values are available as well as experimental data from M€uller et al.11In all cases, except for the c-phases, our structural values have proved to be better than 1% compared to experimental data without taking expansion effects from zero point motions into account.

For the calculation of the force required for a stress

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | DUa | V | Axz | a/2 | b | c |  |
| d o-HfO2 | / | 132.6 | 26.2 | 5.01 | 5.06 | 5.23 | Exp.51 |
| 24 | 138.4 | 26.7 | 5.07 | 5.15 | 5.29 | LDAb |
| 60 | 137.8 | 27.0 | 5.08 | 5.11 | 5.31 | LDA6 |
| 29 | 126.0 | … | … | … | … | LDA48 |
| 65 | 134.1 | 25.4 | 4.92 | 4.96 | 5.16 | GGA48 |
| >25 | 134.4 | 26.5 | 5.02 | 5.08 | 5.27 | GGA49 |
| DUa | V | Axz | a0 | b0 | c0 |

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| induced phase transformation, it is important that the spatial | c c-HfO2 | / | 131.1 | 25.8 | 5.08 | . . . | . . . | Exp.52 |
| orientations of the cells match together for the phase trans- | 137 | 127.3 | 25.3 | 5.03 | . . . | . . . | LDAb |
| formation, and the calculated cell parameters and volumes | 93 | 116.9 | 23.9 | 4.89 | . . . | . . . | LDA47 |
| agree with experimental data at least in their relative values | 152 | 123.0 | . . . | . . . | . . . | . . . | LDA48 |
| to each other. Otherwise values for the necessary pressure or | 237 | 129.6 | 25.6 | 5.06 | . . . | . . . | GGA48 |
| 208 | 127.3 | 25.3 | 5.03 | . . . | . . . | PAW46 |
| stress will be inaccurate. For the plane strain, the cell areas |

in the compressed or expanded planes are relevant. The com-parison of our calculated volume ratios to the experimental volume ratios are summarized in the supplementary material (SI,32Table SII) shows good agreement.

aRelative to m-HfO2.

bThis work.

cValues for 12 atom cell.   
dHalf c-axis.

|  |  |  |
| --- | --- | --- |
| 134109-6 | Materlik, K€unneth, and Kersch | J. Appl. Phys. 117, 134109 (2015) |

TABLE III. Comparison of lattice constants a, b, and c in A˚ and total energy difference DU in meV/f.u. for HZO. Bold values highlight experimental

TABLE IV. Comparison of lattice constants a, b, and c in A˚ and total energy difference DU in meV/f.u. for ZrO2. Bold values highlight experimental

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| results. | | | | | | | | | results. |  |  |  |  |  |  |  |
| Method | | | | | | | | | Structure | DUa(meV) | V (A˚ 3) | Axz (A˚ 2) | a (A˚ ) | b (A˚ ) | c (A˚ ) | Method |
| Structure | DUa(meV) | V (A˚ 3) | Axz (A˚ 2) | a (A˚ ) | b (A˚ ) | | c (A˚ ) | reference | reference |
| m-HZO | 0 | 137.6 | 26.6 | 5.11 | 5.18 | 5.28 | | LDAb | m-ZrO2 | / | 140.3 | 27.0 | 5.15 | 5.20 | 5.32 | Exp.4 |
| DUa | | V | Axz | a0 | c | b0 | | | 0 | 138.2 | 26.6 | 5.11 | 5.20 | 5.28 | LDAb |
| t-HZOc | 70 | 130.3 | 25.4 | 5.04 | 5.13 | a | | LDAb | 0 | 136.6 | 26.3 | 5.09 | 5.20 | 5.24 | LDA47 |
| DUa | | V | Axz | b | a | c | | | 0 | 136.7 | … | … | … | … | LDA48 |
| f-HZO | / | 132.3 | 25.3 | 5.01 | 5.24 | 5.04 | | Exp.11 | 0 | 136.1 | 26.3 | 5.09 | 5.18 | 5.24 | LDA53 |
| 49 | | 132.8 | 25.4 | 5.03 | 5.23 | 5.05 | | LDAb | 0 | 144.7 | 27.4 | 5.20 | 5.28 | 5.35 | GGA48 |
| DUa | | V | Axz | a/2 | b | c | | | 0 | 144.1 | 27.5 | 5.19 | 5.24 | 5.38 | GGA53 |
| o-HZOd | 25 | 137.1 | 26.7 | 5.06 | 5.14 | 5.27 | | LDAb | DUa | V | Axz | a0 | c | b0 |
| DUa | | V | Axz | a0 | b0 | c0 | | |
|  | | | c t-ZrO2 | / | 134.2 | 25.9 | 5.09 | 5.18 | a | Exp.4 |
| c-HZOc | 119 | 127.3 | 25.3 | 5.03 | a | a | | LDAb |
| / | 133.4 | 25.8 | 5.08 | 5.17 | a | Exp.11 |
| aRelative to m-HZO. | | | | | | | | |  |  |  |  |  |  |  |  |
| 49 | 131.3 | 25.5 | 5.05 | 5.15 | a | LDAb |
| bThis work.  c | | | | | | | | | 34 | 130.1 | 25.4 | 5.04 | 5.12 | a | LDA47 |
| Values for 12 atom cell. | | | | | | | | | 38 | 130.4 | … | … | … | … | LDA48 |
| dHalf c-axis. | | | | | | | | |
| 50 | 129.3 | 25.3 | 5.03 | 5.11 | a | LDA53 |
| contribution. The total energy values are only indirectly ac- | | | | | | | | | 109 | 137.9 | 26.3 | 5.13 | 5.21 | a | GGA48 |
| 112 | 138.4 | 26.2 | 5.12 | 5.28 | a | GGA53 |
| cessible in experiments and their consistency can only be | | | | | | | | | DUa | V | Axz | b | a | c |

concluded from the correctness of the final result. LDA results repeatedly in smaller energy differences than GGA calculations. These differences have been systematically studied by Jaffe et al.48for both HfO2 and ZrO2 and by Fadda et al.53for ZrO2 both using ultrasoft pseudopotentials. Considering the total energy, Jaffe et al. concluded that

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| f-ZrO2 | / | 135.5 | 25.8 | 5.07 | 5.26 | 5.08 | Exp.5 |
| 37 | 133.4 | 25.5 | 5.04 | 5.24 | 5.05 | LDAb |
| 34 | 132.1 | 25.3 | 5.02 | 5.22 | 5.04 | LDA47 |
| �60  DUa | 138.1 | 26.1 | 5.10 | 5.30 | 5.11 | LDA6 |
| V | Axz | a/2 | b | c |

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| GGA results are needed since with LDA the phase transfor- | d o-ZrO2 | / | 134.9 | 26.5 | 5.04 | 5.09 | 5.26 | Exp.54 |

mation pressure between the m- and o-phase turned out to be negative. Fadda et al. compared the calculated results with plenty of data sources and found LDA as a better overall description but found too small values for the transition pres-sure between m- and o-phase as well. A comparison of their results for DU in Table IV shows that Jaffe et al. obtained systematically smaller values for all phases and compounds than Fadda et al. Also, their with LDA calculated volume ratios of the structures are not in good agreement with exper-imental results. Therefore, the comparison shows the de-pendence of the correctness of the conclusion on the quality of the pseudopotentials.

The results for DU show consistently positive values for all authors for the stability of f-HfO2. However, Lowther6revealed large negative values for f-ZrO2 and even larger negative values for the o-ZrO2, implying stabil-ity of o-phase. With this single exception, all calculated results lead to same order of increasing total energy values: U(m) < U(o) < U(f) < U(t) < U(c).

C. Helmholtz free energy

To assess the phase stability at a finite temperature T and entropy S, we calculated the Helmholtz free energy F as

F ¼ U � TS; (2)

from the phonon contribution by integrating over the phonon density of state. Fadda53and Zhao56have argued that LDA gives better results for phonon mode frequencies than GGA.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | 25 | 138.7 | 26.8 | 5.07 | 5.20 | 5.27 | LDAb |
| �99  14 | 137.8 | 27.0 | 5.08 | 5.11 | 5.31 | LDA6 |
| 131.9 | … | … | … | … | LDA48 |
| 26 | 130.8 | 26.0 | 4.99 | 5.03 | 5.21 | LDA53 |
| 49 | 138.8 | 26.1 | 5.09 | 5.14 | 5.31 | GGA48 |
| 67 | 138.1 | 26.9 | 5.08 | 5.13 | 5.30 | GGA53 |
| DUa | V | Axz | a0 | b0 | c0 |
| c c-ZrO2 | / | 134.2 | 26.2 | 5.12 | … | … | Exp.55 |
| 120 | 127.3 | 25.3 | 5.03 | … | … | LDAb |
| 82 | 127.3 | 25.3 | 5.03 | … | … | LDA47 |
| 67 | 128.6 | … | … | … | … | LDA48 |
| 94 | 127.3 | 25.3 | 5.03 | … | … | LDA53 |
| 171 | 134.8 | 26.3 | 5.13 | … | … | GGA48 |
| 215 | 134.9 | 26.2 | 5.12 | … | … | GGA53 |

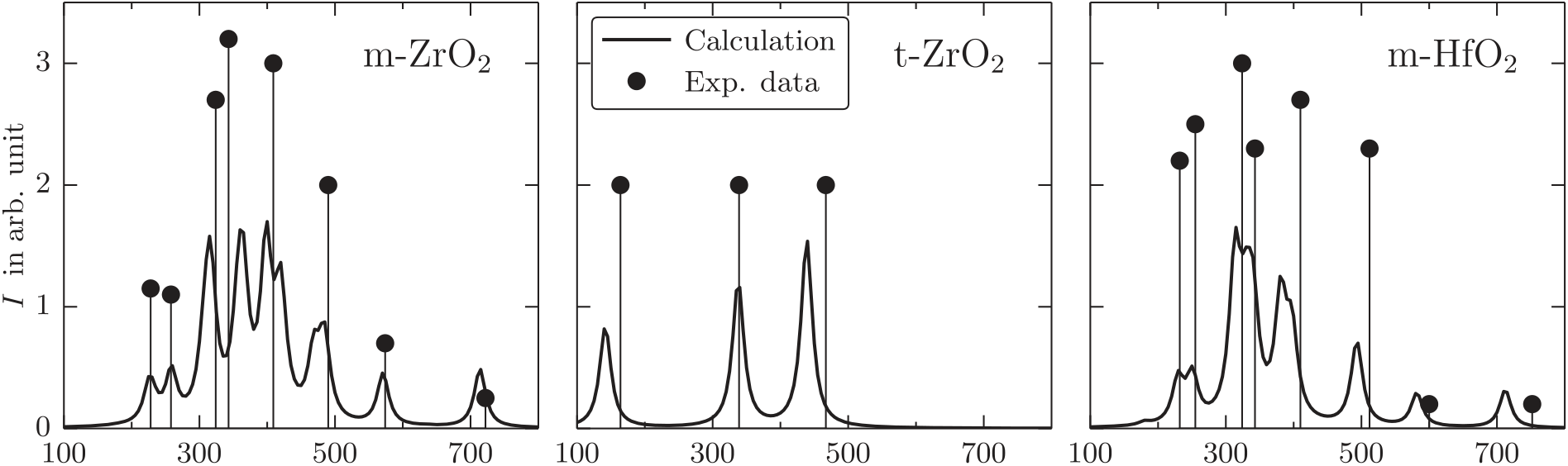
aRelative to m-ZrO2.

bThis work.

cValues for 12 atom cell.   
dHalf c-axis.

The quality of our LDA and the choice of pseudopotentials can be estimated by comparison of the calculated IR-mode frequencies with an experiential IR-absorption spectrum (see Figs. 2(a)–2(c)). With a slight underestimation of the com-puted frequencies, the agreement with experimental data is generally good. The similarity of the structures of Hf1�vZrvO2 becomes visible in the IR-absorption spectrum for v ¼ 0, 0.5 and 1 (see SI,32Fig. S1). The IR-absorption spectra as well as the Raman spectra are fingerprints to identify different phases. The difficulty to distinguish the orthorhombic f- and o-phase from the XRD

|  |  |  |
| --- | --- | --- |
| 134109-7 | Materlik, K€unneth, and Kersch | J. Appl. Phys. 117, 134109 (2015) |



|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |

FIG. 2. Calculated IR-spectrum of (a) m-ZrO2, (b) t-ZrO2, and (c) m-HfO2 in comparison with experimental.58,59

spectrum has been discussed by Howard.57In contrast, according to the ab initio results the t-, f-, and the o-phase might be more easily distinguished using IR- or Raman-spectra instead of XRD (see SI,32Fig. S1(a)–S1(c)).

The results for the Helmholtz free energy difference DF(T) of the phases relative to the m-phase as a function of temperature are shown in Figs. 3(a)–3(c) for HfO2, HZO, and ZrO2. Qualitatively similar results for HfO2, with the excep-tion of the c-phase, have been obtained by Huan49and for ZrO2 by Fadda et al.53with the exception of the f- and c-phase. For all values v in Hf1–vZrvO2, the m-phase has the lowest Helmholtz free energy until the m ! t transition tem-perature (2100 K, 1750 K, and 1250 K for HfO2, HZO, and ZrO2, respectively, compared to 2073 K, 1700 K, and 1300 K in experiments3,34). At a slightly higher temperature (the t ! c transition temperature), the c-phase acquires the lowest Helmholtz free energy (2900 K, 2775 K, and 2650 K in experi-ment3compared to 1950 K, 1550 K, and 1100 K in calculation for HfO2, HZO, and ZrO2, respectively). Our transition tem-peratures for the m ! t transition are in good agreement with experimental data. However, the order of the m ! t and t ! c transformations is reversed in our calculation, indicating either a deficiency of the chosen pseudopotentials for the c-phase or a limited validity of the harmonic approximation for large temperatures. All Helmholtz free energy differences

More important for our paper is the result that neither the f- nor the o-phase becomes favored by a increase in tempera-ture, although the f-phase is only about 50 meV/f.u. and the o-phase only about 25 meV/f.u. less favorable than the m-phase. This is consistent with the results of Huan49for HfO2 and can be understood by an entropy argument: the t- and c-phases lose their higher symmetry faster with increasing thermal motion than the m-, o-, and f-phase and are therefore involved in thermally driven phase transformations. The degree of sym-metry of the m-, o-, and f-phase is the same, measured by the number of symmetry operations per atom (¼0.333), explain-ing their nearly temperature independent Helmholtz free energy difference. Therefore, the o-phase cannot be favored in a thermally driven phase transformation.

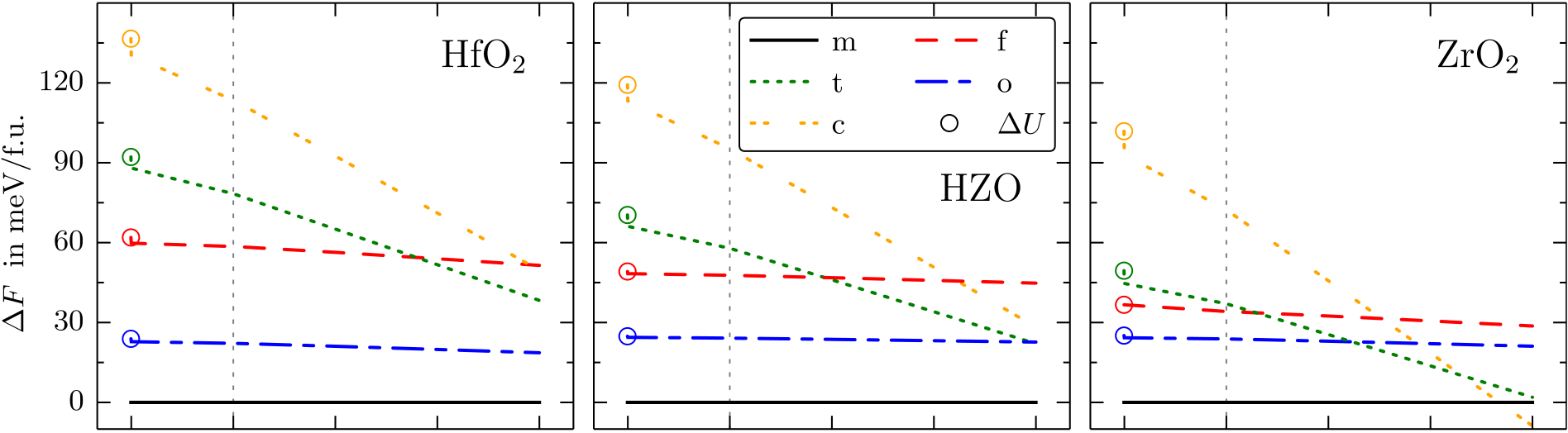
D. Strain and stress Gibbs energy

Since it has been established that temperature does not stabilize the f-phase alone, we now investigate stress effects for a possible stabilization mechanism. Using an isotropic pressure constraint, the phase stability is determined by the Gibbs energy G as

G ¼ F þ pV ¼ U–TS þ pV; (3)

with the pressure p and the volume V. Diamond-anvil cells

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| are larger in HfO2 by about 20% compared to ZrO2. | have | been | used | to | determine | pressure | driven | phase |

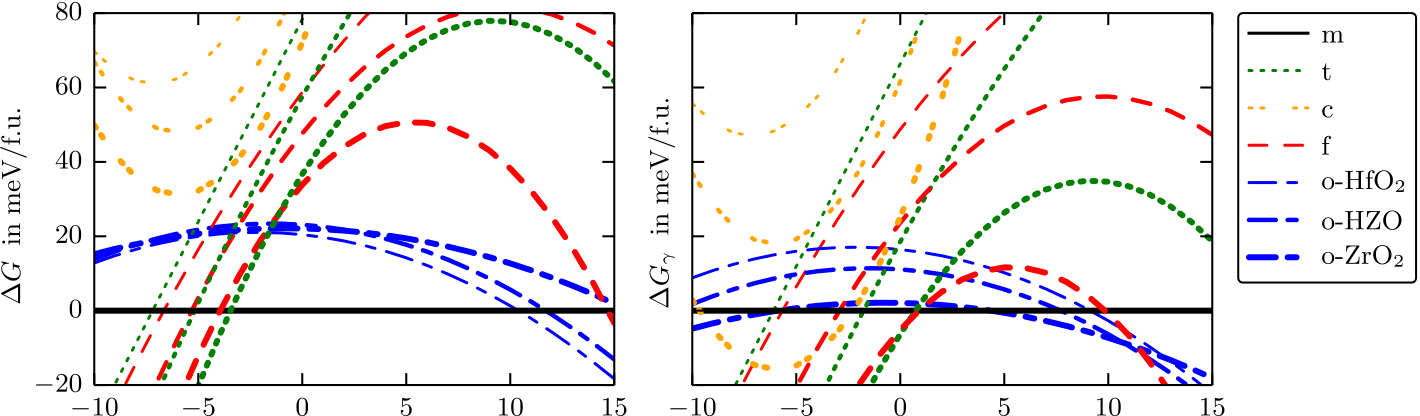


|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |  |  |
|  |

FIG. 3. Calculated total energy differences DU (o) and Helmholtz free energy differences DF(T) relative to the m-phase as a function of temperature for (a)

HfO2, (b) HZO, and (c) ZrO2.

134109-8 Materlik, K€unneth, and Kersch J. Appl. Phys. 117, 134109 (2015)

 around zero pressure and m ! o tran-sition for compressive pressure. (b)

Gibbs energy difference including the

surface energy DGc for 30 nm grains

according to our model.

FIG. 4. (a) Calculated Gibbs energy

difference DG relative to the m-phase

transformations experimentally. For HfO2 36,60 and ZrO2,38,54 strain planes have to be considered while comparing the

the phase transformation from the m-phase to an orthorhom-bic phase has been found between 4 and 12 GPa. After a long dispute, the phase was identified as the o-phase in both cases.4,37To obtain a good value of the m ! o transition pressure in the simulation the total energy difference between the o- and m-phase, and the value of the bulk modu-lus must be calculated accurately enough (Refs. 48 and 53 and discussion in Sec. III B). Our calculated values for tran-sition pressure and bulk modulus compared to experimental data and other calculated values from the literature can be found in SI,32Table SIII. With values between 10 and 15 GPa for the m ! o phase transformation, we obtain a good agreement. The phase transformation pressure has been derived from values of the Gibbs energy difference DG at 300 K relative to the m-phase in Fig. 4(a). The m-phase is stable around zero pressure. For compressive pressure above 10–15 GPa, the o-phase is favored. The t-phase becomes sta-ble for tensile pressures, but the f-phase is never stabilized. The Gibbs energy and hence the transition pressure are modified by effects of the surface energy as known from diamond-anvil experiments with 30 nm small grain material from Ohtaka.54The model for the inclusion of the surface energy to the Gibbs/Helmholtz free energy will be discussed in Subsection III E. Fig. 4(b) illustrates calculated values for a grain size of 30 nm. The surface effects lower the phase transformation pressure.

The fact that the f-phase has only been observed in thin films suggests that the phase could be stabilized under aniso-tropic strain conditions determined from a fixed surface area and zero stress in the normal direction of the film. The stable phase under any strain constraint within the three strain planes xy, xz, and yz is the one with the lowest value of the Helmholtz free energy.61In principle, all combinations of

strain energy of two phases. However, an energy crossover can only happen in spatial orientations of cells with a rough match of lattice constants. For our calculations of the energy crossover under strain, we have chosen the spatial orienta-tions of the 12 atomic cells as shown in Table I. The spatial orientation between the c- and t-phase is obvious, as is the spatial orientation between o- and f-phase. For the t-phase, the c-axis in the crystallographic [001] direction is the largest with 5.15 A˚ and conforms most easily to the a-axis in [100] direction of the f-phase of length 5.25 A˚ . The a- and b-direc-tions of length 5.06 A˚ conform to the b- and c-directions of the f-phase of length 5.04 A˚ and 5.06 A˚ . The remaining two possibilities of a match: transformation (a(t), c(t), b(t)) ! (b(f), a(f), c(f)) (choice in Table I) and c(f)and b(f)inverted are obviously equivalent. Therefore, a t ! f transformation requires only a moderate elongation of the c(t)-axis and no significant modification of the a(t)and b(t)axis and could be promoted with a strain in the xz- or yz-plane. Crucial is the strain energy of the m- and o-phase since these start with the lowest energy from the beginning. The relative orientation between the m- and t-phase has been widely discussed in the literature in context of transformation toughening. Our choice for m ! t in Table I corresponds to the findings of42,43(a(m), b(m), c(m)) ! (a(t), c(t), b(t)). An alternative ori-entation (a(m), b(m), c(m)) ! (a(t), b(t), c(t)) was favored by Luo et al.34while he was looking for the smallest transition barrier between the m- and t-phase. We have calculated the total energy DU for the xz- and yz-strain planes, and all phases for the chosen orientation. The values of the lattice constants and the corresponding cell areas A have been cho-sen by modifying the in plane stress. In equilibrium, the grains should then adopt the crystal phase with the minimum Helmholtz free energy. In Figs. 5(a) and 5(b), we show the

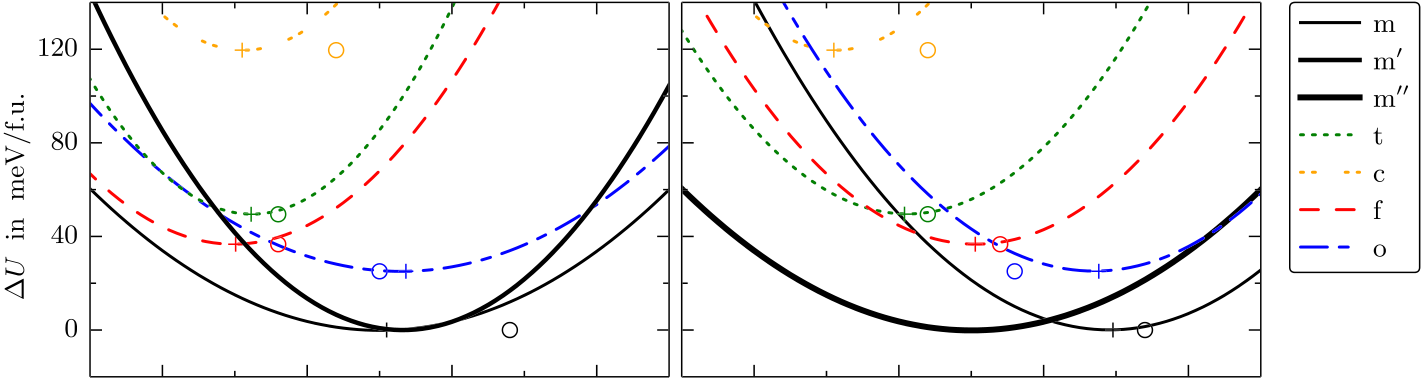


FIG. 5. (a) Calculated DU for all phases with plane strain in the xz-direction. Indicated are the xz-areas from data (o) compared to the xz-areas from the calcula-tion (þ). (b) Calculated DU for all phases with plane strain in the yz-direction. The curves m0represent the m-phase in the orientation chosen by Luo et al.34 and others,47while m refers to our choice in Table I. For comparison, (b) contains the third possible orientation m00which stabilizes the m-phase for all possible strain conditions.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| 134109-9 | Materlik, K€unneth, and Kersch | | | J. Appl. Phys. 117, 134109 (2015)  FIG. 6. (a) Calculated DU for m-, f-, t-,  and o-phases of HZO with plane strain  in the 45�rotated plane. (b) Calculated  DU ZrO2 with plane strain in the 45�  rotated plane. |
|  | | | |
|  |  |  |  |

results as a function of cell area A for ZrO2. For HfO2 and HZO, see SI,32Fig. S2. In our chosen orientation, only a small window of stability occurs for the f-phase in the yz-plane. The crossover point corresponds to a film stress of about 3 GPa in the f-phase and 8 GPa in the m-phase in the yz-plane (label m). No crossover exists in the xz-plane. In the orientation chosen by Luo et al.,34there is a large window of stability in xz-plane, with corresponding plane stress of 9 GPa in the m-phase (label m0) and near zero stress in f-phase. In the yz-plane, both orientations coincide.

To obtain an impartial argument, we have calculated the Helmholtz free energy DF for all strain planes xy, xz, and yz, and all phases. The results can be found in the SI,32Fig. S3.

The conclusion is that a strain induced f-phase is only stable for a compressive strain in the xz-plain when the m-phase orientation of Table I is suppressed for some reason (see Fig. 5(a)). Unfortunately, for such an orientation, the polarization direction is within the thin film plane. Therefore, the grains cannot be polarized by an external electric field perpendicular to the thin film plane and an existing polariza-tion cannot be detected.

So far the strain was oriented in the x, y, and z directions only. Tipping the c-axis out of the plane so that a measurable polarization could remain was suggested by Park.16In Fig. 6, we have calculated how an angle of 45�affects the phase sta-bility by rotating the stress tensor around the x-axis. No dis-tinction between m-phase and m0-phase is necessary, since both orientations fall upon each other. A window of stability opens for the f-phase (compared to Fig. 5), but the crossover points to the m-phase are located at a corresponding stress of 8 GPa for HZO and 7 GPa for ZrO2. Based on the high corre-sponding stress values for crossover points indicated by our calculations, we conclude that the film stress is unlikely the most important factor to cause a phase stabilization of the f-phase with a metastable polarization along the direction

The remaining question is whether the calculations are consistent with the conditions of the first experimental obser-vation of the f-phase in Mg-PSZ (Mg doped, partially stabi-lized zirconium) by Kisi.18The material was described as a matrix of Mg-stabilized c-phase containing grains in the t-phase. Upon cooling, the cubic matrix thermally contracts uniformly, whereas the c-axis of the embedded t-phase grains contracts faster, the a-axis and b-axis slightly slower. This results in a tensile stress condition on the t-phase grains in the c-direction of about 3.6 GPa and a small compressive stress in the a- and b-direction of about 0.5 GPa.

By using the volume V0 of the zero stress cell, the stress tensor rij, and strain tensor sij, we have calculated the aniso-tropic Gibbs energy as

Gi ¼ F þ V0riisii ¼ U – TS þ V0riisii; i ¼ x; y; z; (4)

and the Gibbs energy differences DGi relative to the m-phase for all phases and stress directions, keeping the stress in the orthogonal directions as zero. The results in Fig. 7 show the pressure dependent Gibbs energy at 900 K and 0 K. Since in the experiment, the Mg doping stabilized the enclosed grains in the t-phase at room temperature and above, we assume that the doping shifts the Gibbs energy G of the m-phase above the Gibbs energy G of the t-phase. Reducing the temperature shifts the t-phase up relative to the f-phase due to the entropy contribution TS. In Fig. 7, the f-phase is stabilized at a compressive stress. Our calculations neither included the effects of Mg dopants nor the compressive stress in a and b direction, which might open a larger win-dow of stability for the f-phase. Therefore, we conclude that the computed results are in reasonable agreement with the experimental findings of a f-phase under unidirectional, ten-sile stress conditions. The major conclusion out of this sec-tion is that the f-phase with a measurable polarization in the normal direction cannot be stabilized with compressive film

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| perpendicular to the thin film plane. | | stress alone. | | FIG. 7. (a) Calculated DG relative to the m-phase for all phases and all uni-directional stress directions x, y, and z for ZrO2 at 900 K. The included total energies are from the pure oxide with-out effect of dopant. (b) Calculated DG for ZrO2 at 0 K. The arrows indicate that the m-phase is destabilized in experiments due to Mg-doping.18Stable range of f-phase indicated by (o). |
|  | | | |
|  |  |  |  |

|  |  |  |
| --- | --- | --- |
| 134109-10 | Materlik, K€unneth, and Kersch | J. Appl. Phys. 117, 134109 (2015) |

E. Surface energy and energy crossover

It is known that surface energy effects are responsible for size driven phase transformations on the nanoscale.17An example is the transformation of nanocrystalline ZrO2 from the m- to the t-phase, which is utilized to increase the capaci-tance of nowadays DRAM capacitors. The surface energies c of m- and t-ZrO2 20,21 as well as m-HfO2 23 have been meas-ured, leading to a consensus at least about the range of the val-ues between 2 and 4 J/m2. Surface energies c have also been calculated for various orientations by Christensen22and range between 1.246–2.464 J/m2for m-ZrO2 and 1.239–1.694 J/m2 for t-ZrO2, but the medium surface orientation of the grains is not known. Table V contains a collection of literature results. The surface energy introduces a further dependence in the Helmholtz free energy Fc (or the Gibbs energy Gc, when the pressure is included) and the phase stability of nanocrystals of surface area X is determined from

Fc¼ F þ cX ¼ U – TS þ cX: (5)

The requisite for the existence of t-ZrO2 nanocrystallites is a smaller surface energy compared to the m-phase, which is confirmed by the data in Table V and consistent with a size driven phase transformation and energy crossover below a di-ameter of about 24nm.62In the case of HfO2, the energy cross-over to the t-phase has been observed below about 3 nm.63The surface energy is also dependent on the termination with H or OH (anhydrous or hydrous) or other radicals. As a conse-quence, an exposure of tetragonally stabilized ZrO2 with water could lead to a transformation back to the m-phase, an effect known as low-temperature degradation.64Finally, the surface energies have been measured in powder, whereas many appli-cations use nanocrystalline thin films with additional effects from interface energy. The essential observation in the size driven m ! t transformation in ZrO2 compared to HfO2 is that in HfO2 a much larger surface area to volume ratio is required. This implies a smaller difference between the surface energy of the m- and t-phase in HfO2 compared to ZrO2.

Since our question concerns the stability of the f-phase we need values for the surface energy of all the competing

TABLE V. Surface energy c of Hf1�vZrvO2 for the competing phases from data calculation if available and from our model (bold).

|  |  |  |
| --- | --- | --- |
| c (HfO2) (J/m2) | c (HZO) (J/m2) | c (ZrO2) (J/m2) |

phases which have neither been measured nor calculated. Nonetheless, we need values for the composition depend-ence, since the ferroelectric phase is observed in HZO. We chose the missing values as model parameters. The choice has been guided by the existing data, most importantly by the smaller difference of c (m-HfO2) and c (t-HfO2) com-pared to c (m-ZrO2) and c (t-ZrO2). Additionally, we decrease c with increasing crystal symmetry. The composi-tion dependence finally is modeled from linear interpolation

cðHf1�vZrvO2Þ ¼ ð1 � vÞgðHfO2Þ þ vcðZrO2Þ: (6)

After our choice of values for the surface energy as given in Table V, we now have a complete model to calcu-late the phase stability of Hf1�vZrvO2 and are able to com-pare with existing thin film data. Assuming the absence of a pressure or strain constraint, we determine the stable phase from the minimum of the Helmholtz free energy including the surface contribution Fc ¼ U � TS þ c X. The total energy U and the entropy contribution TS are calculated fun-damentally from DFT as above. At this point, it is clear that these final results depend on the accuracy of the total energy values and entropy contributions, justifying the lengthy dis-cussion above. The surface contribution cX finally uses a phase and composition dependent model parameter c and a geometry model for the calculation of the surface area X, assuming a cylinder surface with height h from film thick-We continue with a comparison of the model results ness and radius r ¼ h/2, if not given otherwise.

with data. Table VI contains the calculated results for a 9 nm thin film at 80 K, 300 K, and a 900 K anneal temperature modeling the experimental results of M€uller.11For all tem-peratures, the 9 nm thick film is calculated to be monoclinic even at anneal temperatures. For smaller crystallites, Shandalov63observed a phase transformation between a size of 7.6 nm and 3.1 nm. For 3.1 nm crystallites, we calculate that f-HfO2 has the lowest Helmholtz free energy in close competition with t-HfO2. Since the crystallites have been annealed, we have calculated the values at 900 K and find t-HfO2 with the lowest Helmholtz free energy. We hypothe-size that such crystallites can be transformed to f-HfO2 under the influence of an E-field. Finally, we calculate the values for crystallites of 2 nm diameter observed by Bohra et al.66 At this small size, we clearly find f-HfO2 to have the lowest Helmholtz free energy. Bohra et al. identified the crystallites to be of o-phase from an electron diffraction pattern. A pos-

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| m-phase, model | 3.4 | 3.2 | 3.0 | sible explanation is that for extremely small crystallites a |
| Data (anhydrous) | 3.7 6 0.123 | 3.45 6 0.2865 | further model is required which adds the effect of size |
| Data (hydrous) | 2.8 6 0.123 | 2.86 6 0.3165 | induced hydrostatic pressure.67,68 |
| Data | 6.4 6 0.220 | The next results in Table VI model the 9 nm thin film |
| … |
| Calculation | 1.246 � 2.46422 | HZO from M€uller et al. at 80 K, 300 K, and 900 K. At 80 K, |
| o-phase, model | 3.3 | |  | | --- | | 2.9 | | |  | | --- | | 2.5 | | f-HZO is stable with an energy of 7 meV/f.u. below the com- |

|  |  |  |  |
| --- | --- | --- | --- |
| f-phase, model | 3.15 | 2.575 | 2.0 |
| t-phase, model | 3.1 | |  | | --- | | 2.5 | | |  | | --- | | 1.9 | |
| Data (anhydrous) | … | … | 1.03 6 0.0565 |
| Data (hydrous) | 1.23 6 0.0465 |
| Data | 2.1 6 0.0520 |
| Calculation | 1.239 � 1.69422 1.8 |
| c-phase, model | 3.05 | 2.425 |

peting t-HZO. At 300 K, the f-HZO is still stable but only 1 meV/f.u. lower than the competing t-HZO. At anneal tem-perature, the t- and c-phase are more favorable, and a phase transformation to the f-phase has to take place upon cooling. The calculations for a 7 nm film show the tendency of a thin-ner film to become tetragonal. The data for a 7 nm film from M€uller2compared to a 9 nm film show this tendency in a

|  |  |  |
| --- | --- | --- |
| 134109-11 | Materlik, K€unneth, and Kersch | J. Appl. Phys. 117, 134109 (2015) |

TABLE VI. Comparison of DFc relative to the m-phase for HfO2 crystallites of different size and temperature in comparison with data. Bold numbers point out the lowest Helmholtz free energy according to our model.

Calculated DFc in meV/f.u.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | | | | | | | |
| T (K) | h/r (nm) | m | o | f | t | c | Observed phase |

HfO2

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| HZO | 300 | Bulk | 0 | 23 | 59 | 78 | 113 | m-phase3 |
| 80 | 9/4.5 | 0 | 11 | 30 | 50 | 83 | m-phase11 |
| 300 | 9/4.5 | 0 | 11 | 29 | 42 | 70 | m-phase11 |
| 900 | 9/4.5 | 0 | 8 | 24 | 16 | 28 | m-phase11 |
| 300 | 7.6/8.0 | 0 | 13 | 34 | 48 | 78 | m-phase63 |
| 300 | 3.1/2.4 | 0 | �6 �9 �36 | 213 | �9  235 | 12 | t-phase63 |
| 900 | 3.1/2.4 | 0 | �18 �88 | 30 | t-phase63 |
| 300 | 2.0/1.0 | 0 | 298 | �92 | o-phase66 |
| 300 | Bulk | 0 | 24 | 48 | 58 | 95 | … |
| 80 | 9/4.5 | 0 | �12 �12 �13 �26 �36 �14 �1  5 | 228 | �21 �27  251 | 19 | f-phase11 |
| 300 | 9/4.5 | 0 | 228 | 1 | f-phase11 |
| 900 | 9/4.5 | 0 | �30 �57 �78  232 | �43 �35 �61 �4  30 | t-phase11 |
| 300 | 7.0/3.5 | 0 | 259 | f,t-phase2 |
| 300 | 5.5/3.0 | 0 | 283 | t-phase16 |
| 300 | 9.2/4.6 | 0 | �31 �1  15 | f-phase16 |
| 300 | 14/7 | 0 | 24 | f-phase16 |
| 300 | 19/9.5 | 0 | 9 | 47 | m-phase16 |
| 300 | 24/12 | 0 | 9 | 17 | 24 | 57 | m-phase16 |

ZrO2

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| 300 | Bulk | 0 | 24 | 34 | 37 | 72 | m-phase3 |
| 80 | 9/4.5 | 0 | �41 �41 �43  0 | �95 �96 �99 �15  1 | 2100 | �63 �84  2137 | t-phase11 |
| 300 | 9/4.5 | 0 | 2106 | t-phase11 |
| 900 | 9/4.5 | 0 | �129  217 | t-phase11 |
| 300 | 24/12 | 0 | 13 | m-phase62 |
| 300 | 36/18 | 0 | 8 | 1 | 33 | m-phase |

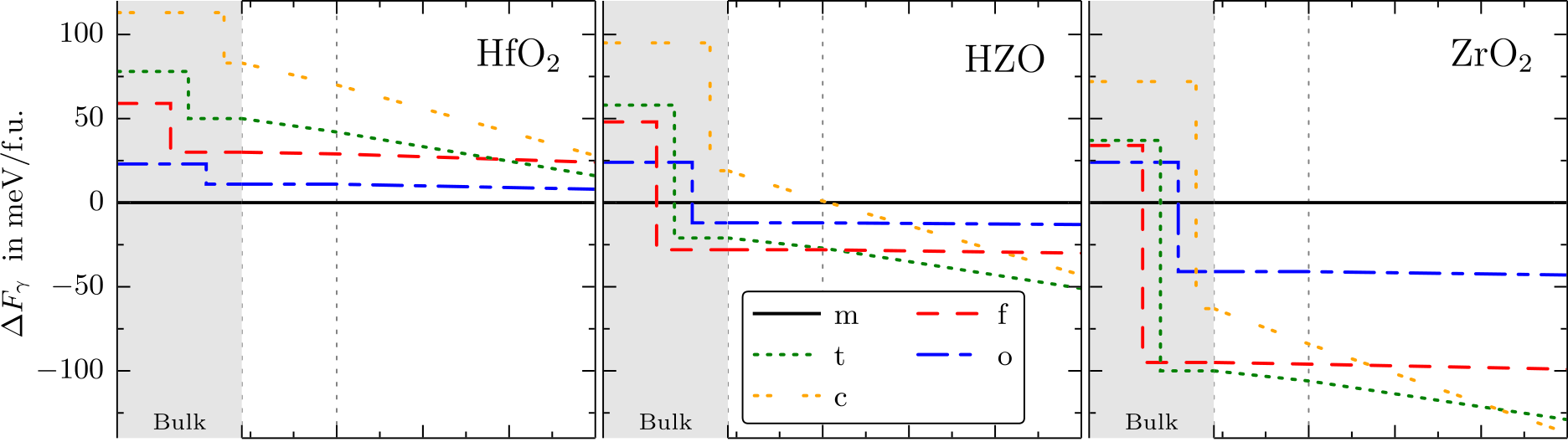
rudimentary antiferroelectric hysteresis curve. This size driven transformation from t- over f- to m-HZO is shown in the calculation and data of Park16who investigated a thick-ness series of 5.5 nm, 9.2 nm, 14 nm, 19 nm, and 24 nm.

The last group of results in Table VI is about ZrO2 start-ing again with a model for the data from M€uller.11The 9 nm film is paraelectric at 80 K and room temperature. The anti-

|  |
| --- |
| ferroelectric character becomes visible in an electric field |

driven paraelectric to ferroelectric phase transformation. The

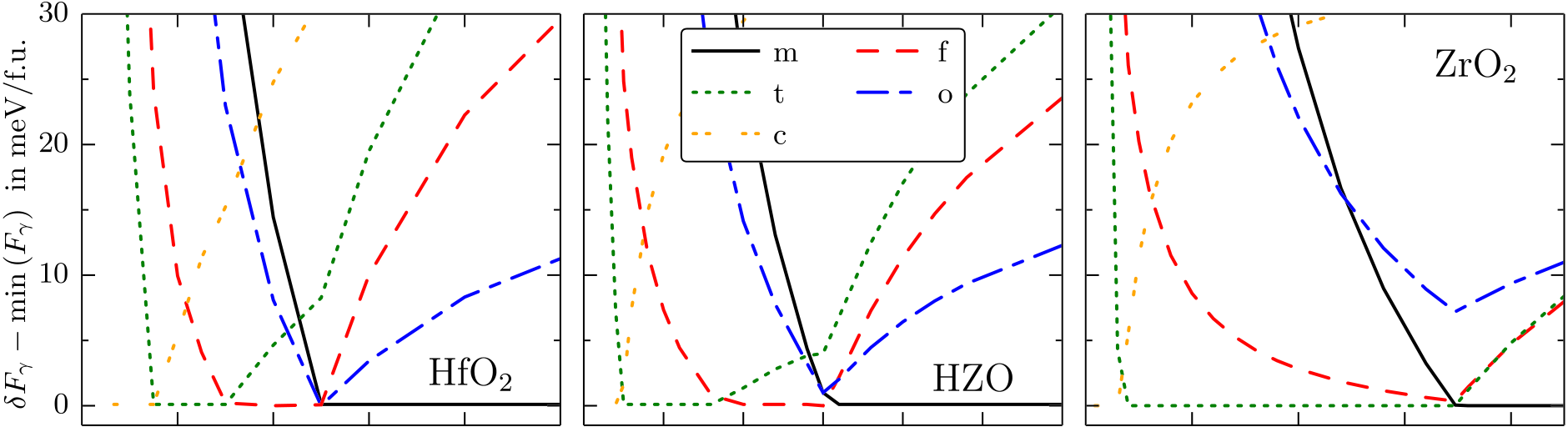
strength of the required electric field in M€uller’s data decreases from about 1 MV/cm to about 0.5 MV/cm when lowering the temperature from 230 K to 80 K. In the calcula-tion, the film shows to be tetragonal in both cases, but the energy difference to the f-phase lowers from 10 meV/f.u. to 5 meV/f.u. which is consistent with a decrease of the required electric field. The last data in the table concern the crossover size from the t- to the m-phase. According to the data of Yashima,62a diameter of 24 nm is sufficient, whereas



|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |  |  |  |

FIG. 8. Calculated Helmholtz free energy DFc for bulk (compare Fig. 3) and a 9 nm polycrystalline film for (a) HfO2, (b) HZO, and (c) ZrO2 above 80 K. The colored area guides the eye to the difference in Helmholtz free energy DF of bulk (intersection with the ordinate) and the 9 nm thin film at 80 K.

|  |  |  |
| --- | --- | --- |
| 134109-12 | Materlik, K€unneth, and Kersch | J. Appl. Phys. 117, 134109 (2015) |



|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |
|  |  |  |

FIG. 9. Calculated free energy difference DFc relative to the phase with minimal Helmholtz free energy at 300 K as a function of film thickness for (a) HfO2, (b) HZO, and (c) ZrO2. A window of stability for the f-phase arises for HfO2 from 3 nm to 5 nm and in HZO from 8 nm and 16 nm thin film strength.

in the model a size of 36 nm is necessary to yield the m-phase to have the lowest energy.

The results of the free energy model for the 9 nm film data series of M€uller11in comparison with bulk free energy is shown in Fig. 8. HfO2 is monoclinic for all temperatures. HZO is ferroelectric for room temperature and below. ZrO2 is tetragonal for all temperatures. The ferroelectricity in HZO arises in the model from the linear dependence of the surface energy on the composition and the increase of the surface energy with crystal symmetry.

The conclusion from the comparison of the Helmholtz free energy model with available data is that the model describes the observations very well, although the involved energy differences are in the order of a few meV/f.u. This is possible with a model, where the error from the total energy contribution U and the error from the entropy contribution TS have been reduced to a small amount.

As a consequence, the model achieves a predictive capa-bility. Fig. 9 shows the modeled Helmholtz free energy for the phases of HfO2, HZO, and ZrO2 relative to the phase with the lowest Helmholtz free energy at these conditions as a function of film thickness with cylindrical grains.

The crossover of HfO2 from the high symmetry phases to the low symmetric m-phase happens for film thickness

below 5 nm. The model predicts ferroelectric HfO2 for a grain size between 3 nm and 5 nm, for smaller grains the t-phase and c-phase. For HZO, a similar crossover exists but is shifted to larger grain size. The ferroelectric films exist in the thickness regime between 8 nm and 16 nm. Thinner films or smaller grains occur in the t-phase. In addition, our model suggests the existence of a ferroelectric phase in epitaxial HZO below a critical film strength of about 5 nm. For ZrO2, the large surface energy difference of the t-phase is dominant such that no f-phase is stable, although it is energetically close. The energy disadvantage to the t-phase is small so that it can be overcome with an electric field (see Sec. III F). Despite being the second most stable phase in the bulk, the o-phase is never the most stable phase for any grain volume.

F. Electric enthalpy and field driven phase transformation

1 The antiferroelectric behavior observed in doped HfO2 and ZrO2 11 has been interpreted as a field induced phase transformation.19We examine the consistency of this state-ment with the Helmholtz free energy model containing a contribution for a polarized crystal in an electric field as

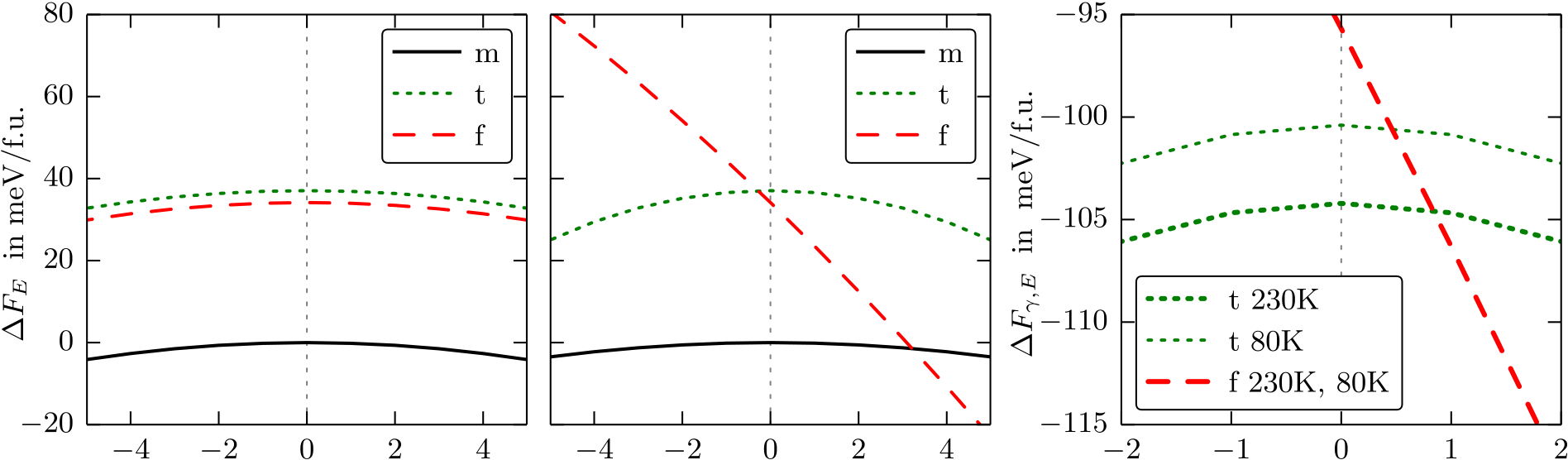
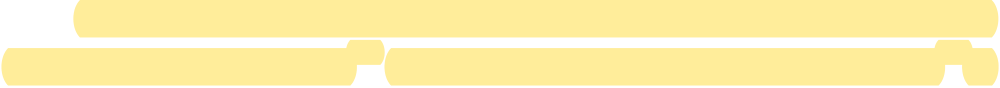


FIG. 10. Calculated Helmholtz free energy difference DFc,E for bulk ZrO2 relative to the m-phase at zero E-field and T ¼ 300 K, (a) for an E-field in y-direc-

tion, (b) for an E-field in z-direction and a polarization P in negative z-direction. (c) Shift of the energy crossover in 9 nm ZrO2 for the same E-field/polarization

configuration for a temperature increase from T ¼ 80 K to T ¼ 230 K. For the t-phase, the Helmholtz free energy difference to the m-phase DFc,E is dependent on temperature, while for the f-phase it is nearly independent on temperature (see Fig. 3).



|  |  |  |
| --- | --- | --- |
| 134109-13 | Materlik, K€unneth, and Kersch | J. Appl. Phys. 117, 134109 (2015) |

described by Souza.69The Helmholtz free energy in a vol-ume V0 with the field energy contribution is

TABLE VII. Diagonal elements of the dielectric tensor and averaged dielec-tric constants calculated from the Helmholtz free energy and from a linear response calculation.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Fc;E ¼ Fc � V0DE ¼ U – TS þ cX � V0DE; | (7) | HfO2 | HZO | ZrO2 |

when D ¼ D(E) ¼ ere0E þ P is the electric displacement as a function of the macroscopic electric field E, which has the

polarization P as a permanent contribution and ere0E as an

induced contribution where er is the dielectric tensor. The

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| eE-field | eionic | etotal | eionic | etotal | eionic | etotal |

m-phase P14

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| x | 20.0 | 19.8 | 24.7 | 21.5 | 26.7 | 23.3 | 29.0 |
| y | 18.0 | 18.1 | 22.9 | 19.6 | 24.8 | 21.3 | 27.0 |

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| total energy is obtained from a structural relaxation of the | z | 15.0 | | 15.0 | 19.5 | 15.6 | … | 20.5 | 16.3 | 21.5 |
| supercell including the field term. An induced polarization | R/3 | | 17.7 | 17.7 | 22.4 | 18.9 | 24.1 | 20.3 | 25.8 |
| lowers the energy, while the field strain of the crystal | o-phase P61 | | |
| 20.3 | 25.3 | 23.7 | 29.5 |
| increases U. A further effect is a modification of the entropy | x | … | |
| from the field strain shifted phonon modes. However, we | y | … | | 18.0 | 22.8 | 26.0 | … | 31.5 | 21.6 | 27.3 |
| z | … | | 15.5 | 20.1 | … | 16.8 | 22.1 |
| have neglected this contribution. |
| R/3 | | … | 17.9 | 22.7 | … | 20.7 | 26.3 |
| We have calculated the Helmholtz free energy FE for |
| f-phase P29 | | |
| ZrO2 bulk in the m-, t-, and f-phase and show the differ- | 23.8 | 28.8 | 28.4 | 34.4 |
| x | 24.0 | |
| ence relative to the m-phase at zero E-field in Figs. 10(a) |
| y | 19.0 | | 19.3 | 24.2 | 20.7 | 25.9 | 22.1 | 27.8 |
| and 10(b). A field in y-direction orthogonal to the polariza- |
| z | 26.0 | | 23.1 | 28.0 | 24.6 | 29.9 | 26.1 | 31.7 |
| tion direction does not lead to a phase transformation for |
| R/3 | | 23.0 | 22.1 | 27.0 | 23.8 | 29.1 | 25.5 | 31.3 |
| realizable fields. A field in the z-direction parallel to the | t-phase P137 | | | 51.8 | 56.9 | 54.3 | 60.4 | 55.4 | 61.5 |
| polarization lowers the Helmholtz free energy of the f- | x,z | 55.0 | |
| y | 20.0 | | 19.2 | 24.0 | 19.9 | 25.3 | 19.9 | 25.3 |
| phase significantly by about 10 meV/f.u. for 1 MV/cm. For |

bulk ZrO2, a field of about 4 MV/cm would be required to

|  |
| --- |
| give the f-phase a Helmholtz free energy below the m- |

|  |
| --- |
| phase. |

But for thin film ZrO2, the Helmholtz free energy of the t- and f-phase is already below the m-phase. Here, a much lower field of about 1 MV/cm is sufficient for the f-phase to obtain the lowest energy. We can reproduce the temperature dependence of the field driven phase transformation in 9 nm thin films measured by M€uller11by calculating the change of the entropy contribution with temperature. In Fig. 10(c), we show the Helmholtz free energy of the t- and f-phase for 80 K and 230 K. At 80 K, a field strength of only 0.5 MV/cm is sufficient to induce the phase transformation.

The necessary E-field for the field driven phase transfor-mation from the t- to the f-phase was so far determined from the Helmholtz free energy difference Fc,E(f-phase) � Fc,E(t-phase) in an equilibrium state. A further requirement for a

|  |
| --- |
| phase transformation is a sufficiently low energy barrier to |

the new Helmholtz free energy minimum. As a good approx-imation to the transition barrier,34we have calculated the maximum of the transition path from the t- to the f-phase. We obtain a barrier of only 30 meV/f.u. for the chosen orien-tation in Table I. Such a small barrier should be overcome by

|  |
| --- |
| thermal energy alone, hence removal of the external field |

relaxes the structure back to the t-phase.

Similar values have been recently found in the literature (30 meV/f.u. in Huan49and 30 meV/f.u. from Reyes-Lillo47). The low barrier is related to a soft phonon mode interpolat-

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| R/3 | 43.3 | 40.9 | 45.9 | 42.8 | 48.7 | 43.6 | 49.4 |

c-phase P225

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| x,y,z | … | 30.9 | 36.0 | … | 41.5 | 47.6 |
| R/3 | … | 30.9 | 36.0 | … | 41.5 | 47.6 |
| i¼x,y,z (diagonal elements of the dielectric tensor) and the polarization P from a second order fit to the computed values | | | | | | |

of the field energy V0 DE¼ V0(ere0E þ P)E. Table VII shows the comparison of these values eE-field for m-, f-, and t-HfO2 with values eionic from a conventional linear response calcula-tion to an ionic perturbation and etotal including the electronic contribution. The results only show a small deviation between

eE-field and eionic indicating a slightly nonlinear behavior.

The comparison of the extracted polarization PE-field for f-HfO2 with values PBerry from a conventional Berry phase calculation is shown in Table VIII. The values match excel-

lent. Furthermore, the table shows the dependence of the

polarization P of Hf1–vZrvO2 on the stoichiometry v. The polarization increases with Zr content. This can be under-

stood by the increasing values of the Born charges obtained

from the linear response calculation. Table VIII shows only

the diagonal values of the Born charge tensor. A simplified

TABLE VIII. Polarization.

|  |  |  |
| --- | --- | --- |
| HfO2 | HZO | ZrO2 |

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| ing between t- and f-phase. Reyes-Lillo et al. found a total |  | PE-field |  | PBerry |  | PBerry |  | PBerry |  |
| 0.505 | 0.504 | 0.541 | 0.579 |
| energy difference of only 1 meV between f- and t-phase and |  |  |  |  |  |  |  |  |  |
| |  | | --- | | calculated a critical field strength of 1.2 MV/cm necessary to | | z | eE-field | Dz |  | Z | Dz | Z | Dz | Z |

overcome the barrier of 30 meV/f.u. They do not explain why the f-phase relaxes back into the t-phase, after the field strength is reduced to zero.

To show the consistency of the Helmholtz free energy calculation, we have extracted the dielectric constants eri,

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Zr | 20.0 | 0.003 | 5.08 | 0.002 | 5.23 | 0.002 | 5.85 |
| O1 | 18.0 | �0.138 0.008 | � 2.53 2.52 | �0.135 0.008 | –2.54 2.58 | �0.133 0.006 | –2.58 2.60 |
| O2 | 15.0 |
| Equation (1) | 17.7 | 0.67 | | 0.69 | | 0.72 | |

|  |  |  |
| --- | --- | --- |
| 134109-14 | Materlik, K€unneth, and Kersch | J. Appl. Phys. 117, 134109 (2015) |

estimation based on Eq. (1) including the diagonal values and a perturbation in z-direction around the centrosymmetric configuration leads to a good estimation and explains the stoichiometric trend of the polarization.

IV. CONCLUSION

In this paper, we have investigated the origin of the fer-roelectricity in Hf1�vZrvO2 for HZO with v ¼ 0.5, and the origin of antiferroelectricity for ZrO2 with DFT calculations and a phenomenological model for the surface energy contri-bution. From total energy calculations, we found that the bulk ferroelectric phase Pca21 is not stable. The computa-tions for several polymorphs were compared to a number of literature results to estimate the theoretical uncertainty and find the most reliable method. We decided for the LDA func-tional and norm-conserving TM pseudopotentials. The tem-perature dependent Helmholtz free energy was calculated accordingly. As a first possible mechanism to stabilize the ferroelectric phase we investigated the film strain. Although we could reproduce all relevant stress and strain dependent phenomena in HfO2 and ZrO2 with our model, we only

|  |
| --- |
| found a small window of rather high compressive film strain |

to allow a stabilization of the ferroelectric phase. Since the thus stabilized structure has a polarization in the strain plane, which is unobservable, we found the stress/strain mechanism unlikely to be the major cause of the stabilization. As a sec-ond possible mechanism, we investigated the surface energy contribution to the Helmholtz free energy. Since the surface energy of ferroelectric grains has not been measured or cal-culated so far we build a phenomenological model for all polymorphs and all stoichiometry values by interpolating between existing values using decreasing values for increas-ing crystal symmetry. With the Gibbs/Helmholtz free energy model containing an ab initio computed part for total energy, entropy, stress, or strain, and a phenomenological part for the surface energy, we could reproduce the observed phases for nanosized thin films and grains and found stable ferro-electric HZO in a size window around 10 nm at room tem-perature in the absence of strain. Based on the model, we furthermore predict a similar ferroelectric window in HfO2 around 4 nm and below 5 nm in epitaxial HZO. For ZrO2, no stable ferroelectric nanosized grains exist. After calculating the field dependent contribution to the Helmholtz free energy self-consistently, we found an electric field of about 1 MV/ cm sufficient to give ferroelectric grains of 9 nm at room temperature the lowest Helmholtz free energy. Furthermore, reducing the temperature favors the stability and decreases the crossover field in accordance with experimental data.

ACKNOWLEDGMENTS

The author wants to thank U. Schroeder and T. Schenk from NamLab and U. B€ottger and S. Starschich from RWTH Aachen for discussions. The German Research Foundation (Deutsche Forschungsgemeinschaft) is acknowledged for funding this research in the frame of the project “Inferox”

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| (Project | No. | MI | 1247/11-1). | The | authors | gratefully |

acknowledge the Gauss Centre for Supercomputing e.V. ([www.gauss-centre.eu](http://www.gauss-centre.eu/)) for funding this project by providing

computing time on the GCS Supercomputer SuperMUC at Leibniz Supercomputing Centre (LRZ, www.lrz.de).

1T. S. B€oscke, J. M€uller, D. Br€auhaus, U. Schr€oder, and U. B€ottger,“Ferroelectricity in hafnium oxide thin films,” [Appl. Phys. Lett.](http://dx.doi.org/10.1063/1.3634052) 99(10), 102903 (2011).

2J. M€uller, T. S. B€oscke, D. Br€auhaus, U. Schr€oder, U. B€ottger, J. Sundqvist, P. K€ucher, T. Mikolajick, and L. Frey, “Ferroelectric Zr0.5Hf0.5O2 thin films for nonvolatile memory applications,” [Appl. Phys. Lett.](http://dx.doi.org/10.1063/1.3636417) 99(11), 112901 (2011).

3J. Wang, H. P. Li, and R. Stevens, “Hafnia and hafnia-toughened ceram-ics,” [J. Mater. Sci.](http://dx.doi.org/10.1007/BF00541601) 27(20), 5397–5430 (1992).

4E. H. Kisi and C. J. Howard, “Crystal structures of zirconia phases and their inter-relation,” [KEM](http://dx.doi.org/10.4028/www.scientific.net/KEM.153-154.1) 153–154, 1–36 (1998).

5E. H. Kisi, C. J. Howard, and R. J. Hill, “Crystal structure of orthorhombic zirconia in partially stabilized zirconia,” [J. Am. Ceram. Soc.](http://dx.doi.org/10.1111/j.1151-2916.1989.tb06322.x) 72(9), 1757–1760 (1989).

6J. Lowther, J. Dewhurst, J. Leger, and J. Haines, “Relative stability of ZrO2 and HfO2 structural phases,” [Phys. Rev. B](http://dx.doi.org/10.1103/PhysRevB.60.14485) 60(21), 14485–14488 (1999).

7J. H. Choi, Y. Mao, and J. P. Chang, “Development of hafnium based high-k materials—A review,” [Mater. Sci. Eng. R](http://dx.doi.org/10.1016/j.mser.2010.12.001) 72(6), 97–136 (2011). 8S. Mueller, J. Mueller, A. Singh, S. Riedel, J. Sundqvist, U. Schroeder, and T. Mikolajick, “Incipient ferroelectricity in Al-doped HfO2 thin films,” [Adv. Funct. Mater.](http://dx.doi.org/10.1002/adfm.201103119) 22(11), 2412–2417 (2012).

9T. Olsen, U. Schr€oder, S. M€uller, A. Krause, D. Martin, A. Singh, J. M€uller, M. Geidel, and T. Mikolajick, “Co-sputtering yttrium into hafnium oxide thin films to produce ferroelectric properties,” [Appl. Phys. Lett.](http://dx.doi.org/10.1063/1.4747209) 101(8), 082905 (2012).

10M. H. Park, Y. H. Lee, H. J. Kim, Y. J. Kim, T. Moon, D. D. Kim, J. M€uller, A. Kersch, U. Schroeder, T. Mikolajick, and C. S. Hwang,“Ferroelectricity and Antiferroelectricity of Doped Thin HfO2-based Films,” [Adv. Mater.](http://dx.doi.org/10.1002/adma.201404531) 27, 1811 (2015).

11J. M€uller, T. S. B€oscke, U. Schr€oder, S. Mueller, D. Br€auhaus, U. B€ottger, L. Frey, and T. Mikolajick, “Ferroelectricity in simple binary ZrO2 and HfO2,” [Nano Lett.](http://dx.doi.org/10.1021/nl302049k) 12(8), 4318–4323 (2012).

12J. Muller, T. S. Boscke, U. Schroder, R. Hoffmann, T. Mikolajick, and L. Frey, “Nanosecond polarization switching and long retention in a novel MFIS-FET based on ferroelectric HfO2,” [IEEE Electron Device Lett.](http://dx.doi.org/10.1109/LED.2011.2177435) 33(2), 185–187 (2012).

13J. M€uller, U. Schr€oder, T. S. B€oscke, I. M€uller, U. B€ottger, L. Wilde, J. Sundqvist, M. Lemberger, P. K€ucher, T. Mikolajick, and L. Frey,“Ferroelectricity in yttrium-doped hafnium oxide,” [J. Appl. Phys.](http://dx.doi.org/10.1063/1.3667205) 110(11), 114113 (2011).

14D. Zhou, J. M€uller, J. Xu, S. Knebel, D. Br€auhaus, and U. Schr€oder,“Insights into electrical characteristics of silicon doped hafnium oxide fer-roelectric thin films,” [Appl. Phys. Lett.](http://dx.doi.org/10.1063/1.3688915) 100(8), 082905 (2012).

15J. Robertson, “High dielectric constant gate oxides for metal oxide Si tran- sistors,” [Rep. Prog. Phys.](http://dx.doi.org/10.1088/0034-4885/69/2/R02) 69(2), 327–396 (2006).

16M. Hyuk Park, H. Joon Kim, Y. Jin Kim, T. Moon, and C. Seong Hwang,

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| “The | effects | of | crystallographic | orientation | and | strain | of | thin |

Hf0.5Zr0.5O2 film on its ferroelectricity,” [Appl. Phys. Lett.](http://dx.doi.org/10.1063/1.4866008) 104(7), 072901 (2014).

17R. C. Garvie, “The occurrence of metastable tetragonal zirconia as a crys- tallite size effect,” [J. Phys. Chem.](http://dx.doi.org/10.1021/j100888a024) 69(4), 1238–1243 (1965).

18E. H. Kisi, “Influence of hydrostatic pressure on the t [!](http://dx.doi.org/10.1111/j.1151-2916.1998.tb02402.x) o transformation in Mg-PSZ studied by in situ neutron diffraction,” [J. Am. Ceram. Soc.](http://dx.doi.org/10.1111/j.1151-2916.1998.tb02402.x)  81(3), 741–745 (1998).

19T. S. B€oscke, St. Teichert, D. Br€auhaus, J. M€uller, U. Schr€oder, U. B€ottger, and T. Mikolajick, “Phase transitions in ferroelectric silicon doped hafnium oxide,” [Appl. Phys. Lett.](http://dx.doi.org/10.1063/1.3636434) 99(11), 112904 (2011).

20M. W. Pitcher, S. V. Ushakov, A. Navrotsky, B. F. Woodfield, G. Li, J. Boerio-Goates, and B. M. Tissue, “Energy crossovers in nanocrystalline zirconia,” [J. Am. Ceram. Soc.](http://dx.doi.org/10.1111/j.1551-2916.2004.00031.x) 88(1), 160–167 (2005).

21S. V. Ushakov, A. Navrotsky, Y. Yang, S. Stemmer, K. Kukli, M. Ritala, M. A. Leskel€a, P. Fejes, A. Demkov, C. Wang, B.-Y. Nguyen, D. Triyoso, and P. Tobin, “Crystallization in hafnia- and zirconia-based systems,”[phys. Status Solidi B](http://dx.doi.org/10.1002/pssb.200404935) 241(10), 2268–2278 (2004).

22A. Christensen and E. Carter, “First-principles study of the surfaces of zirconia,” [Phys. Rev. B](http://dx.doi.org/10.1103/PhysRevB.58.8050) 58(12), 8050–8064 (1998).

23W. Zhou, S. V. Ushakov, T. Wang, J. G. Ekerdt, A. A. Demkov, and A. Navrotsky, “Hafnia: Energetics of thin films and nanoparticles,” [J. Appl. Phys.](http://dx.doi.org/10.1063/1.3435317) 107(12), 123514 (2010).

|  |  |  |
| --- | --- | --- |
| 134109-15 | Materlik, K€unneth, and Kersch | J. Appl. Phys. 117, 134109 (2015) |

24M. Hyuk Park, H. Joon Kim, Y. Jin Kim, W. Lee, T. Moon, and C. Seong Hwang, “Evolution of phases and ferroelectric properties of thin Hf0.5Zr0.5O2 films according to the thickness and annealing temperature,”[Appl. Phys. Lett.](http://dx.doi.org/10.1063/1.4811483) 102(24), 242905 (2013).

25X. Gonze, “A brief introduction to the ABINIT software package,” [Z.](http://dx.doi.org/10.1524/zkri.220.5.558.65066)  [Kristallogr.](http://dx.doi.org/10.1524/zkri.220.5.558.65066) 220, 558 (2005).

26X. Gonze, B. Amadon, P.-M. Anglade, J.-M. Beuken, F. Bottin, P. Boulanger, F. Bruneval, D. Caliste, R. Caracas, M. C^ot�e, T. Deutsch, L. Genovese, P. Ghosez, M. Giantomassi, S. Goedecker, D. R. Hamann, P. Hermet, F. Jollet, G. Jomard, S. Leroux, M. Mancini, S. Mazevet, M. Oliveira, G. Onida, Y. Pouillon, T. Rangel, G.-M. Rignanese, D. Sangalli, R. Shaltaf, M. Torrent, M. J. Verstraete, G. Zerah, and J. W. Zwanziger, “ABINIT: First-principles approach to ma-terial and nanosystem properties,” [Comput. Phys. Commun.](http://dx.doi.org/10.1016/j.cpc.2009.07.007) 180(12), 2582–2615 (2009).

27M. Fuchs and M. Scheffler, “Ab initio pseudopotentials for electronic structure calculations of poly-atomic systems using density-functional the-ory,” [Comput. Phys. Commun.](http://dx.doi.org/10.1016/S0010-4655(98)00201-X) 119(1), 67–98 (1999).

28D. Porezag, M. Pederson, and A. Liu, “Importance of nonlinear core cor-rections for density-functional based pseudopotential calculations,” [Phys. Rev. B](http://dx.doi.org/10.1103/PhysRevB.60.14132) 60(20), 14132–14139 (1999).

29H. J. Monkhorst and J. D. Pack, “Special points for Brillouin-zone integra- tions,” [Phys. Rev. B](http://dx.doi.org/10.1103/PhysRevB.13.5188) 13(12), 5188–5192 (1976).

30X. Gonze, “Dynamical matrices, Born effective charges, dielectric permit-tivity tensors, and interatomic force constants from density-functional per-turbation theory,” [Phys. Rev. B](http://dx.doi.org/10.1103/PhysRevB.55.10355) 55(16), 10355–10368 (1997).

31A. Rappe, K. Rabe, E. Kaxiras, and J. Joannopoulos, “Optimized pseudopotentials,” [Phys. Rev. B](http://dx.doi.org/10.1103/PhysRevB.41.1227) 41(2), 1227–1230 (1990).

32See supplementary material at <http://dx.doi.org/10.1063/1.4916707> for additional data sets concerning structural data, IR spectra, stress and strain, surface energy, and polarization.

33W. Zheng, K. H. Bowen, J. Li, I. Dabkowska, and M. Gutowski,“Electronic structure differences in ZrO2 vs HfO2,” [J. Phys. Chem. A](http://dx.doi.org/10.1021/jp053593e) 109(50), 11521–11525 (2005).

34X. Luo, W. Zhou, S. Ushakov, A. Navrotsky, and A. Demkov,“Monoclinic to tetragonal transformations in hafnia and zirconia: A com-bined calorimetric and density functional study,” [Phys. Rev. B](http://dx.doi.org/10.1103/PhysRevB.80.134119) 80(13), 134119 (2009).

35H. Arashi, “Pressure-induced phase transformation of HfO2,” [J. Am.](http://dx.doi.org/10.1111/j.1151-2916.1992.tb04149.x)  [Ceram. Soc.](http://dx.doi.org/10.1111/j.1151-2916.1992.tb04149.x) 75(4), 844–847 (1992).

36Y. Al-Khatatbeh, K. K. M. Lee, and B. Kiefer, “Phase diagram up to 105

46Q. Zeng, A. R. Oganov, A. O. Lyakhov, C. Xie, X. Zhang, J. Zhang, Q. Zhu, B. Wei, I. Grigorenko, L. Zhang, and L. Cheng, “Evolutionary search for new high-k dielectric materials: methodology and applications to hafnia-based oxides,” [Acta Crystallogr. C](http://dx.doi.org/10.1107/S2053229613027861) 70(2), 76–84 (2014).

47S. E. Reyes-Lillo, K. F. Garrity, and K. M. Rabe, “Antiferroelectricity in thin-film ZrO2 from first principles,” [Phys. Rev. B](http://dx.doi.org/10.1103/PhysRevB.90.140103) 90(14), 140103 (2014). 48J. Jaffe, R. Bachorz, and M. Gutowski, “Low-temperature polymorphs of ZrO2 and HfO2: A density-functional theory study,” [Phys. Rev. B](http://dx.doi.org/10.1103/PhysRevB.72.144107) 72(14), 144107 (2005).

49T. D. Huan, V. Sharma, G. A. Rossetti, and R. Ramprasad, “Pathways towards ferroelectricity in hafnia,” [Phys. Rev. B](http://dx.doi.org/10.1103/PhysRevB.90.064111) 90(6), 064111 (2014). 50I. MacLaren, T. Ras, M. MacKenzie, A. J. Craven, D. W. McComb, and S. de Gendt, “Texture, twinning, and metastable “tetragonal” phase in ultrathin films of HfO2 on a Si substrate,” [J. Electrochem. Soc.](http://dx.doi.org/10.1149/1.3141705) 156(8), G103 (2009). 51R. Suyama, H. Takubo, and S. Kume, “Synthesis of Hf1-xZrxO2,” [J. Am.](http://dx.doi.org/10.1111/j.1151-2916.1985.tb15797.x)  [Ceram. Soc.](http://dx.doi.org/10.1111/j.1151-2916.1985.tb15797.x) 68(9), C237 (1985).

52I. A. El-Shanshoury, V. A. Rudenko, and I. A. Ibrahim, “Polymorphic behavior of thin evaporated films of zirconium and hafnium oxides,”[J. Am. Ceram. Soc.](http://dx.doi.org/10.1111/j.1151-2916.1970.tb12090.x) 53(5), 264–268 (1970).

53G. Fadda, G. Zanzotto, and L. Colombo, “First-principles study of the effect of pressure on the five zirconia polymorphs. I. Structural, vibra- tional, and thermoelastic properties,” [Phys. Rev. B](http://dx.doi.org/10.1103/PhysRevB.82.064105) 82(6), 064105 (2010). 54O. Ohtaka, T. Yamanaka, S. Kume, N. Hara, H. Asano, and F. Izumi, “Structural analysis of orthorhombic ZrO2 by high resolution neutron powder diffraction,” [Proc. Jpn. Acad. Ser. B: Phys. Biol. Sci.](http://dx.doi.org/10.2183/pjab.66.193) 66(10), 193–196 (1990). 55F. Namavar, G. Wang, C. L. Cheung, R. F. Sabirianov, X. C. Zeng, W. N. Mei, J. Bai, J. R. Brewer, H. Haider, and K. L. Garvin, “Thermal stability of nanostructurally stabilized zirconium oxide,” [Nanotechnology](http://dx.doi.org/10.1088/0957-4484/18/41/415702) 18(41), 415702 (2007).

56X. Zhao and D. Vanderbilt, “First-principles study of structural, vibra-tional, and lattice dielectric properties of hafnium oxide,” [Phys. Rev. B](http://dx.doi.org/10.1103/PhysRevB.65.233106) 65(23), 233106 (2002).

57C. J. Howard, E. H. Kisi, and O. Ohtaka, “Crystal structures of two ortho- rhombic zirconias,” [J. Am. Ceram. Soc.](http://dx.doi.org/10.1111/j.1151-2916.1991.tb08307.x) 74(9), 2321–2323 (1991).

58C. Pecharrom�an, M. Oca~na, and C. J. Serna, “Optical constants of tetrag-onal and cubic zirconias in the infrared,” [J. Appl. Phys.](http://dx.doi.org/10.1063/1.363218) 80(6), 3479 (1996).

59D. A. Neumayer and E. Cartier, “Materials characterization of ZrO2–SiO2 and HfO2–SiO2 binary oxides deposited by chemical solution deposition,”[J. Appl. Phys.](http://dx.doi.org/10.1063/1.1382851) 90(4), 1801 (2001).

60O. Ohtaka, T. Yamanaka, S. Kume, N. Hara, H. Asano, and F. Izumi,

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| GPa and mechanical strength of HfO2,” [Phys. Rev. B](http://dx.doi.org/10.1103/PhysRevB.82.144106) 82(14), 144106 | “Structural | analysis | of | orthorhombic | hafnia | by | neutron | powder |

(2010).

37J. Leger, P. Tomaszewski, A. Atouf, and A. Pereira, “Pressure-induced structural phase transitions in zirconia under high pressure,” [Phys. Rev. B](http://dx.doi.org/10.1103/PhysRevB.47.14075) 47(21), 14075–14083 (1993).

38Y. Al-Khatatbeh, K. K. M. Lee, and B. Kiefer, “Phase relations and hardness trends of ZrO2 phases at high pressure,” [Phys. Rev. B](http://dx.doi.org/10.1103/PhysRevB.81.214102) 81(21), 214102 (2010).

39K. Momma and F. Izumi, “VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data,” [J. Appl. Crystallogr.](http://dx.doi.org/10.1107/S0021889811038970) 44(6), 1272–1276 (2011).

40H. T. Stokes and D. M. Hatch, “FINDSYM: program for identifying the space-group symmetry of a crystal,” [J. Appl. Crystallogr.](http://dx.doi.org/10.1107/S0021889804031528) 38(1), 237–238 (2005).

41A. G. Jackson, Handbook of Crystallography: For Electron Microscopists and Others (Springer, New York, NY, 1991).

42K. Negita and H. Takao, “Condensations of phonons at the tetragonal to monoclinic phase transition in ZrO2,” [J. Phys. Chem. Solids](http://dx.doi.org/10.1016/0022-3697(89)90495-2) 50(3), 325–331 (1989).

43D. Simeone, G. Baldinozzi, D. Gosset, M. Dutheil, A. Bulou, and T. Hansen, “Monoclinic to tetragonal semireconstructive phase transition of zirconia,” [Phys. Rev. B](http://dx.doi.org/10.1103/PhysRevB.67.064111) 67(6), 064111 (2003).

44G. Csonka, J. Perdew, A. Ruzsinszky, P. Philipsen, S. Lebe`gue, J. Paier, O. Vydrov, and J.�Angy�an, “Assessing the performance of recent density functionals for bulk solids,” [Phys. Rev. B](http://dx.doi.org/10.1103/PhysRevB.79.155107) 79(15), 155107 (2009).

45R. Ruh and P. W. R. Corfield, “Crystal structure of monoclinic hafnia and com-parison with monoclinic zirconia,” [J. Am. Ceram. Soc.](http://dx.doi.org/10.1111/j.1151-2916.1970.tb12052.x) 53(3), 126–129 (1970).

diffraction,” [J. Am. Ceram. Soc.](http://dx.doi.org/10.1111/j.1151-2916.1995.tb08391.x) 78(1), 233–237 (1995).

61O. Di�eguez, K. Rabe, and D. Vanderbilt, “First-principles study of epitax- ial strain in perovskites,” [Phys. Rev. B](http://dx.doi.org/10.1103/PhysRevB.72.144101) 72(14), 144101 (2005).

62M. Yashima and S. Tsunekawa, “Structures and the oxygen deficiency of

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| tetragonal | and | monoclinic | zirconium | oxide | nanoparticles,” | [Acta](http://dx.doi.org/10.1107/S0108768105030570) |

[Crystallogr. B: Struct. Sci.](http://dx.doi.org/10.1107/S0108768105030570) 62(1), 161–164 (2006).

63M. Shandalov and P. C. McIntyre, “Size-dependent polymorphism in HfO2 nanotubes and nanoscale thin films,” [J. Appl. Phys.](http://dx.doi.org/10.1063/1.3243077) 106(8), 084322 (2009).

64J. Chevalier, L. Gremillard, A. V. Virkar, and D. R. Clarke, “The tetragonal-monoclinic transformation in zirconia: Lessons learned and future trends,” [J. Am. Ceram. Soc.](http://dx.doi.org/10.1111/j.1551-2916.2009.03278.x) 92(9), 1901–1920 (2009).

65A. V. Radha, O. Bomati-Miguel, S. V. Ushakov, A. Navrotsky, and P. Tartaj, “Surface enthalpy, enthalpy of water adsorption, and phase stability in nanocrystalline monoclinic zirconia,” [J. Am. Ceram. Soc.](http://dx.doi.org/10.1111/j.1551-2916.2008.02796.x) 92(1), 133–140 (2009).

66F. Bohra, B. Jiang, and J.-M. Zuo, “Textured crystallization of ultrathin haf-nium oxide films on silicon substrate,” [Appl. Phys. Lett.](http://dx.doi.org/10.1063/1.2724925) 90(16), 161917 (2007).

67W. G. Wolfer, “Elastic properties of surfaces on nanoparticles,” [Acta](http://dx.doi.org/10.1016/j.actamat.2011.08.033)  [Mater.](http://dx.doi.org/10.1016/j.actamat.2011.08.033) 59(20), 7736–7743 (2011).

68B. Santara, P. K. Giri, K. Imakita, and M. Fujii, “Microscopic origin of lat-tice contraction and expansion in undoped rutile TiO2 nanostructures,”[J. Phys. D: Appl. Phys.](http://dx.doi.org/10.1088/0022-3727/47/21/215302) 47(21), 215302 (2014).

69I. Souza, J. [�](http://dx.doi.org/10.1088/0022-3727/47/21/215302)I~niguez, and D. Vanderbilt, “First-principles approach to insu- lators in finite electric fields,” [Phys. Rev. Lett.](http://dx.doi.org/10.1103/PhysRevLett.89.117602) 89(11), 117602 (2002).