

This is the accepted manuscript made available via CHORUS, the article has been published as:

## Prediction of Semimetallic Tetragonal $\text{Hf}_2\text{O}_3$ and $\text{Zr}_2\text{O}_3$ from First Principles

Kan-Hao Xue, Philippe Blaise, Leonardo R. C. Fonseca, and Yoshio Nishi

Phys. Rev. Lett. **110**, 065502 — Published 5 February 2013

DOI: [10.1103/PhysRevLett.110.065502](https://doi.org/10.1103/PhysRevLett.110.065502)

# Prediction of semi-metallic tetragonal $\text{Hf}_2\text{O}_3$ and $\text{Zr}_2\text{O}_3$ from first-principles

Kan-Hao Xue,<sup>1</sup> Philippe Blaise,<sup>2</sup> Leonardo R. C. Fonseca,<sup>3</sup> and Yoshio Nishi<sup>4</sup>

<sup>1</sup>*IMEP-LAHC, Minatec-INPG, 3 rue Parvis Louis Néel,*

*BP 257, 38016 Grenoble Cedex 1, France*

<sup>2</sup>*CEA, LETI, Minatec Campus, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France*

<sup>3</sup>*Center for Semiconductor Devices, State University of Campinas, Campinas, SP, Brazil*

<sup>4</sup>*Department of Electrical Engineering,*

*Stanford University, Stanford, CA 94305, USA*

## Abstract

Tetragonal semi-metallic phases are predicted for  $\text{Hf}_2\text{O}_3$  and  $\text{Zr}_2\text{O}_3$  using density functional theory. The structures belong to space group  $P\bar{4}m2$  and are more stable than their corundum counterparts. Many body corrections at first order confirm their semi-metallic character. The carrier concentrations are very similar for both materials, and are estimated as  $1.8 \times 10^{21} \text{ cm}^{-3}$  for both electrons and holes, allowing for electric conduction. This could serve as a basic explanation for the low resistance state of hafnia-based resistive random access memory (RRAM).

Hafnia ( $\text{HfO}_2$ ) and zirconia ( $\text{ZrO}_2$ ) are found in a number of important technological applications.<sup>1,2</sup> In particular, hafnia has become a key component in sub-micrometer silicon MOS technology as the present choice of high permittivity dielectric layer.<sup>3</sup> In addition, it is also a promising candidate material for resistive random access memory (RRAM), which is one of the leading technologies for the next-generation non-volatile memory.<sup>4-7</sup> The core element of RRAM is a metal/insulator/metal capacitor which is subject to an electroforming process, where a high electric field (some MV/cm) is applied across the capacitor to create conduction paths in the insulating thin film, here named filaments. These filaments are of unknown composition or shape, and can be easily disturbed under electrical stress, leading to a memory effect. Knowing the composition of the filaments is crucial to the understanding of RRAM's physics. Previous work on  $\text{TiO}_2$  RRAM reveals that the conductive filament is possibly due to  $\text{Ti}_n\text{O}_{2n-1}$  Magnéli phases, where the value of  $n$  is mostly 4 or 5.<sup>8</sup> For hafnia RRAM, the structure of the conductive filaments has not been reported, though it is widely accepted that the filaments are associated with an oxygen-deficient phase.<sup>9,10</sup> Since the impact of electroforming is expected to occur in small and random patches of the capacitor, experimental investigation of the filaments suffers from great difficulty.

In this paper we employ first-principles density functional theory<sup>11</sup> (DFT) calculations to identify metallic O-poor stable compositions of hafnium and zirconium oxides, which may be reachable from room temperature normal pressure monoclinic  $\text{Hf}(\text{Zr})\text{O}_2$  [ $m\text{-Hf}(\text{Zr})\text{O}_2$ ] with the assistance of an external source of energy, possibly an applied electric field. While the processing and operation of oxide-based RRAM stimulated our search of a conductive phase in these materials, our predictions are quite general and should have broader implications in materials and device physics.

For our DFT calculations we employed the plane-wave based Vienna *Ab initio* Simulation Package (VASP)<sup>12</sup> with projector augmented-wave (PAW) pseudopotentials<sup>13</sup> including Hf 5*p*, 5*d* and 6*s* (Zr 4*s*, 4*p*, 4*d* and 5*s*) electrons and O 2*s* and 2*p* electrons in the valence. Generalized gradient approximation (GGA) was used for the exchange-correlation energy, within the Perdew-Burke-Ernzerhof (PBE) functional.<sup>14</sup> The plane wave energy cutoff is chosen as 500 eV which converges for all the involved compounds, and sufficiently dense Monkhorst-Pack<sup>15</sup> or  $\Gamma$ -centered (for *h.c.p.* structures)  $k$ -mesh was utilized for sampling the Brillouin zone.

Since DFT/GGA usually underestimates band gaps,<sup>16</sup> and may even deem a material metallic rather than semiconductor as the case of bulk germanium,<sup>17</sup> for the metal candidates we calculated the first order energy shifts with GW approximation<sup>18</sup> ( $G_0W_0$ ) using the ABINIT<sup>19,20</sup> program.

Hf (Zr) semi-core electrons were explicitly included through the  $5s^2 5p^6 5d^2 6s^2$  ( $4s^2 4p^6 4d^2 5s^2$ ) configuration while core electrons were replaced by Troullier-Martins pseudopotentials.<sup>21</sup> Convergence was achieved with 360 bands and a 15 Ha cutoff for the wave functions employed in the evaluation of the dielectric function and the  $\Sigma$  function. A plasmon-pole approximation<sup>22</sup> was used.

The  $m$ -Hf(Zr)O<sub>2</sub> unit cells were fully relaxed until all Hellmann-Feynman forces were less than 0.01 eV/Å and all stresses were less than 400 MPa. The relaxed  $m$ -Hf(Zr)O<sub>2</sub> unit cell parameters are  $a=5.146$  (5.219) Å,  $b/a=1.010$  (1.012),  $c/a=1.036$  (1.036) and  $\beta = 99.68^\circ$  (99.68°), close to experimental values:<sup>23</sup>  $a=5.117$  (5.151) Å,  $b/a=1.011$  (1.010),  $c/a=1.034$  (1.032) and  $\beta = 99.22^\circ$  (99.20°). The formation enthalpy of  $m$ -Hf(Zr)O<sub>2</sub> calculated with respect to *h.c.p.* Hf (Zr) and an isolated O<sub>2</sub> molecule is -1166 (-1106) kJ/mol, after adopting (throughout this paper) the 1.36 eV energy correction for the O<sub>2</sub> molecule provided by Wang *et al.*<sup>24</sup> These results are in accordance with the experimental values, which are -1145 kJ/mol for hafnia and -1101 kJ/mol for zirconia.<sup>25</sup>

We look for a conductive state in  $m$ -Hf(Zr)O<sub>2</sub> by increasing the concentration of oxygen vacancies in the materials. To serve as reference we first calculated the formation energies of single and double oxygen vacancies in a 96-atom  $m$ -Hf(Zr)O<sub>2</sub> supercell ( $2 \times 2 \times 2$ ). Only the neutral oxygen vacancy was considered since our ultimate goal is an energetically favorable metallic phase, where charged point defects are not stable. There are two inequivalent O sites regarding O coordination, namely the 3- and 4-coordinated O(A) and O(B) sites, respectively. The formation

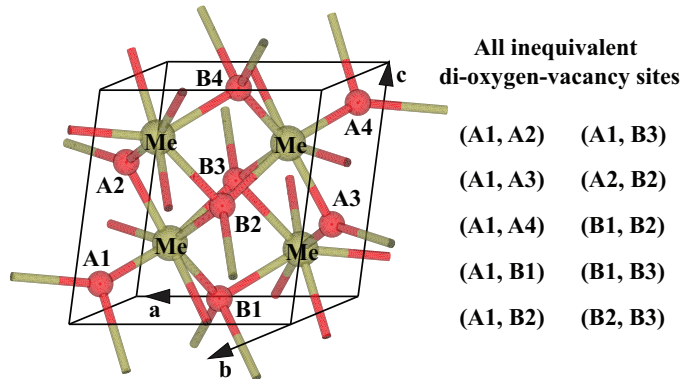


FIG. 1: Unit cell used for calculations of the formation energy of oxygen vacancies in MeO<sub>2</sub> (Me = Hf or Zr) with all metal and oxygen sites identified. The ten inequivalent pairs of oxygen sites are also listed.

energy of a neutral oxygen vacancy is defined as

$$E_{\text{for}} = E_{\text{D}} - E_0 + \mu_{\text{O}} \quad (1)$$

where  $E_{\text{D}}$  is the energy of the defective supercell,  $E_0$  is the energy of the defect-free supercell and  $\mu_{\text{O}}$  is the chemical potential of oxygen. Under oxygen-rich condition  $\mu_{\text{O}}$  is usually set as one half of that of an  $\text{O}_2$  molecule. In this case the calculated  $E_{\text{for}}$  for a neutral O(A) vacancy in  $m\text{-Hf}(\text{Zr})\text{O}_2$  is 7.13 (6.62) eV, while for a neutral O(B) vacancy it is 7.00 (6.53) eV. The difference between the two formation energies, 0.13 (0.09) eV, is similar to Zheng *et al.*,<sup>26</sup> but larger than Foster *et al.* who reported a 0.02 eV difference in both cases.<sup>27, 28</sup> Next we calculated the formation energies of di-oxygen-vacancy pairs in  $m\text{-Hf}(\text{Zr})\text{O}_2$ . To this end, the eight oxygen sites in a unit cell were named A1–A4 and B1–B4, as shown in Fig. 1. The distance between two di-oxygen-vacancy pairs is around 10 Å, casting them as isolated pairs. Since  $m\text{-Hf}(\text{Zr})\text{O}_2$  possesses the baddeleyite structure with space group  $P2_1/c$ , there are ten inequivalent di-oxygen-vacancy pairs. The most energetically favorable pair is (B1, B2), whose formation energy per vacancy is the same as of a single O(B) vacancy.

Under usual experimental conditions the dielectric is placed between two metal electrodes where oxygen can migrate as an interstitial. We thus calculated the incorporation energies of oxygen in bulk *h.c.p.* Ti and *f.c.c.* Pt, two commonly used electrodes. The results are -6.24 eV and 0.91 eV, respectively. In Tab. I we compare the formation energies of isolated single and double oxygen vacancies in  $m\text{-Hf}(\text{Zr})\text{O}_2$  resulting in the release of  $\text{O}_2$  or the incorporation of O interstitial in the two metals. Notice that the formation energy of a neutral O(B) vacancy in  $m\text{-Hf}(\text{Zr})\text{O}_2$  plus an oxygen interstitial in *h.c.p.* Ti is merely 0.76 (0.29) eV, which is attributed to the strong Ti–O bonding.

Next, O-deficient  $\text{Hf}(\text{Zr})\text{O}_x$  with different stoichiometries were studied in the search for the dielectric-metal transition. We began with the  $\text{Hf}(\text{Zr})_4\text{O}_7$  models generated by introducing one oxygen vacancy per 12-atom  $m\text{-Hf}(\text{Zr})\text{O}_2$  for two inequivalent cases, *i.e.*, O(A) and O(B). The defective unit cells were fully relaxed until all Hellmann-Feynman forces were less than 0.01 eV/Å. Atomic coordinates, cell dimensions and shape were subject to relaxation. The formation energies per vacancy of the two  $\text{Hf}(\text{Zr})_4\text{O}_7$  phases are almost the same as in the single oxygen vacancy cases. The resulting densities of states (DOS) are shown in Figs. 2(b) and 2(c). The calculated band gaps are similar to  $m\text{-Hf}(\text{Zr})\text{O}_2$  [Fig. 2(a)], around 4.0 (3.5) eV compared with experimental values 5.8 (5.4) eV.<sup>29, 30</sup> Since the band gap is underestimated by DFT/GGA, a more accurate

calculation employing many-body techniques can only push  $\text{Hf}(\text{Zr})_4\text{O}_7$  even farther from a metal. Moreover, Figs. 2(b) and 2(c) show that a fully occupied defect-induced band emerges in the band gap which cannot account for the measured metallic state in hafnia-based RRAM where the resistance is on the order of hundreds of Ohms for 10 nm thick films.<sup>31</sup> However, the trend does hint at a possible dielectric-to-metal phase transition for stronger off-stoichiometric hafnia or zirconia.

Chemical formula	Vacancy site(s)	Supercell units	Formation energy (eV/vacancy)		
			with oxygen going to		
			O <sub>2</sub>	Ti	Pt
<hr/>					
Single oxygen vacancy					
Me <sub>32</sub> O <sub>63</sub>	O(A)	2×2×2	7.13(6.62)	0.89(0.38)	8.04(7.53)
Me <sub>32</sub> O <sub>63</sub>	O(B)	2×2×2	7.00(6.53)	0.76(0.29)	7.91(7.44)
<hr/>					
Closest di-oxygen-vacancy					
Me <sub>32</sub> O <sub>62</sub>	(B1, B2)	2×2×2	7.01(6.52)	0.77(0.28)	7.92(7.43)
Me <sub>32</sub> O <sub>62</sub>	(B2, B3)	2×2×2	7.02(6.60)	0.78(0.36)	7.93(7.51)
Me <sub>32</sub> O <sub>62</sub>	(A1, B1)	2×2×2	7.03(6.53)	0.79(0.29)	7.94(7.44)
<hr/>					
Me <sub>4</sub> O <sub>7</sub>					
Me <sub>4</sub> O <sub>7</sub>	O(A)	1×1×1	7.16(6.66)	0.92(0.42)	8.07(7.57)
Me <sub>4</sub> O <sub>7</sub>	O(B)	1×1×1	7.03(6.57)	0.79(0.33)	7.94(7.48)
<hr/>					
Me <sub>2</sub> O <sub>3</sub>					
Me <sub>4</sub> O <sub>6</sub>	(B1, B2)	1×1×1	6.55(5.66)	0.31(-0.58)	7.46(6.57)
Me <sub>4</sub> O <sub>6</sub>	(A1, B1)	1×1×1	6.92(6.40)	0.68(0.16)	7.83(7.31)
Me <sub>4</sub> O <sub>6</sub>	(B2, B3)	1×1×1	6.95(6.33)	0.71(0.09)	7.86(7.24)

TABLE I: Formation energies of isolated single oxygen vacancies and di-oxygen-vacancy pairs, and of substoichiometric  $\text{Hf}(\text{Zr})_4\text{O}_7$  and  $\text{Hf}(\text{Zr})_2\text{O}_3$  in different structures derived from monoclinic  $\text{HfO}_2$  and  $\text{ZrO}_2$ . Me stands for  $\text{Hf}(\text{Zr})$ .

	<i>a</i>	<i>c</i>	Hf <sub>z</sub>	O(A) <sub>z</sub>	Bulk modulus
Hf <sub>2</sub> O <sub>3</sub>	3.135 Å	5.646 Å	0.2553	0.1351	246 GPa
Zr <sub>2</sub> O <sub>3</sub>	3.174 Å	5.763 Å	0.2525	0.1367	228 GPa

TABLE II: Calculated structural parameters of tetragonal  $\text{Hf}_2\text{O}_3$  and  $\text{Zr}_2\text{O}_3$ .

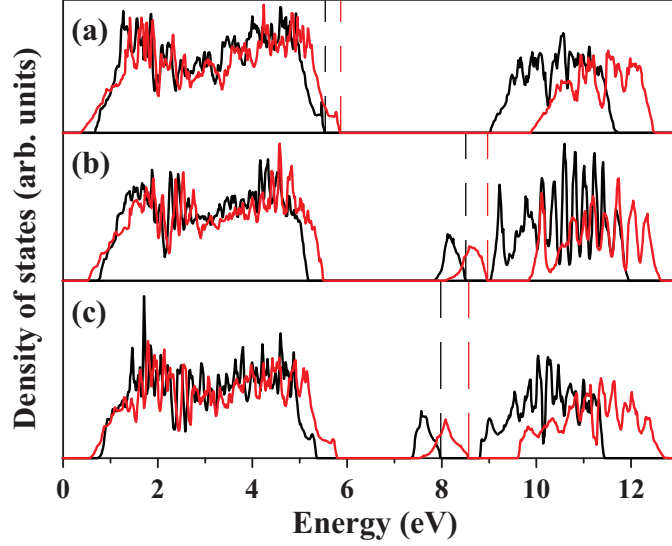


FIG. 2: Density of states for (a)  $m\text{-Hf(Zr)O}_2$ ; (b)  $\text{Hf(Zr)}_4\text{O}_7$  with one O(A) vacancy; (c)  $\text{Hf(Zr)}_4\text{O}_7$  with one O(B) vacancy. Black curves are for Zr-based compounds while red curves are for Hf-based compounds. All figures are aligned horizontally with respect to the O 2s band (not shown). The highest occupied molecular orbital levels are indicated by vertical dashed lines.

Hence, several  $\text{Hf(Zr)}_2\text{O}_3$  models were set up with two oxygen vacancies per 12-atom  $m\text{-Hf(Zr)O}_2$  unit cell. For all inequivalent cases (Fig. 1) the cells remain monoclinic during relaxation of the unit cell vectors, except for the (B1, B2) case which suffers from a monoclinic-to-tetragonal transition. The tetragonal  $\text{Hf(Zr)}_2\text{O}_3$  [ $t\text{-Hf(Zr)}_2\text{O}_3$ ] phase (Fig. 3; structural parameters in Tab. II) is the ground state of all ten  $\text{Hf(Zr)}_2\text{O}_3$  candidates. It belongs to the  $D_{2d}$  point group and  $P\bar{4}m2$  (No. 115) space group<sup>33</sup>. Symmetry analysis indicates that Hf (Zr) and 2/3 of the oxygen sites [named O(A)] are at the  $2g$  position while 1/3 of the oxygen sites [named O(B)] are at the  $1c$  position<sup>34</sup>. The Hf (Zr) coordination number is 7 as in  $m\text{-Hf(Zr)O}_2$ , while O(A) and O(B) have coordination numbers 5 and 4, respectively. The average Hf(Zr)–O(A) and Hf(Zr)–O(B) bond lengths are 2.295 (2.322) Å and 2.089 (2.134) Å, respectively, compared with 2.084 (2.117) Å and 2.209 (2.240) Å in  $m\text{-Hf(Zr)O}_2$ . Bader analysis reveals less charge transfer from Hf (Zr) to O in  $t\text{-Hf(Zr)}_2\text{O}_3$  than in  $m\text{-Hf(Zr)O}_2$ . The Hf (Zr) charge changes from 2.73e (2.57e) in  $m\text{-Hf(Zr)O}_2$  to 2.10e (2.02e) in  $t\text{-Hf(Zr)}_2\text{O}_3$ ; the O(A) charge changes from -1.34e (-1.25e) to -1.39e (-1.34e); and the O(B) charge changes from -1.39e (-1.31e) to -1.41e (-1.37e).

Figure 4 shows the band diagram and orbital-projected DOS of  $t\text{-Hf}_2\text{O}_3$ . Results for  $t\text{-Zr}_2\text{O}_3$  (not shown) are similar. The high symmetry points in the Brillouin zone are named according

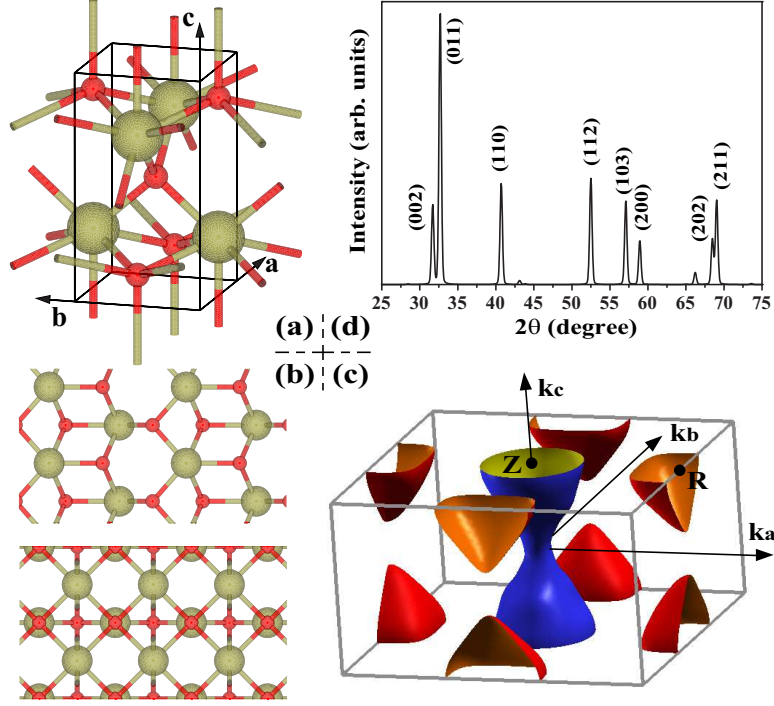


FIG. 3: Tetragonal  $\text{Hf}_2\text{O}_3$  and  $\text{Zr}_2\text{O}_3$ .<sup>32</sup> (a) Primitive cell with 5 atoms; (b) view along  $a$ -axis (upper) and  $c$ -axis (lower); (c) Fermi surface of  $\text{Hf}_2\text{O}_3$  at  $T=0$  K; (d) simulated powder X-ray diffraction patterns of  $\text{Hf}_2\text{O}_3$ . Big green balls: Hf or Zr; small red balls: O.

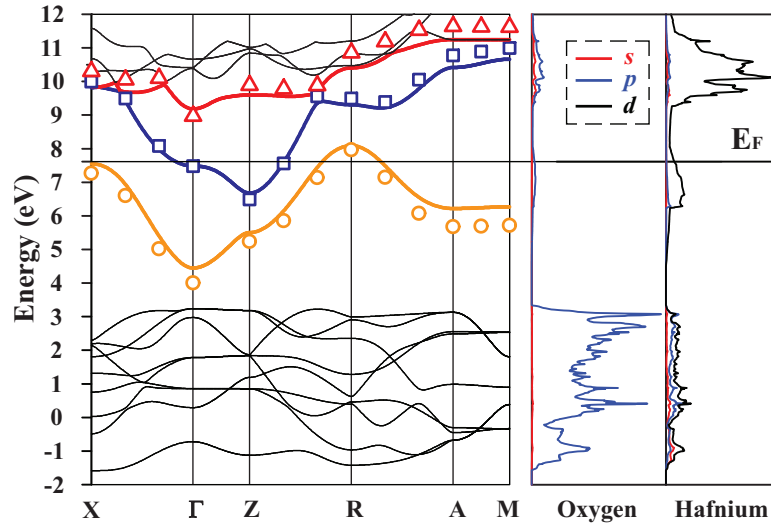


FIG. 4: Tetragonal  $\text{Hf}_2\text{O}_3$  electronic band structure (left) and orbital projected DOS (right). DFT/GGA (solid lines) and  $G_0W_0$  (discrete marks) band structures are superimposed and aligned by their Fermi levels. Results for tetragonal  $\text{Zr}_2\text{O}_3$  (not shown) are similar.



to the Bilbao crystallographic server.<sup>33</sup> A semi-metallic behavior is revealed in the overlap of the partially occupied valence band top and conduction band bottom located at the different high symmetry points R and Z, respectively. Both band edges are mostly derived from Hf 5*d* states. The semi-metallic character of the two compounds was confirmed by  $G_0W_0$  calculations of the many-body correction to the DFT/GGA energy levels. As shown in Fig. 4, the energy shifts are small, of the order of a few tenths of eV. From the calculated band structures the densities of conduction electrons and holes can be obtained by integrating their occupation of the blue and orange bands shown in Fig. 4, respectively. The electron and hole densities are both  $1.8 \times 10^{21} \text{ cm}^{-3}$ , below  $10^{22} \text{ cm}^{-3}$  which sets the upper limit for semi-metals, but substantially larger than common semi-metals such as Bi, Sb and As, with carrier concentrations  $3 \times 10^{17} \text{ cm}^{-3}$ ,  $5 \times 10^{19} \text{ cm}^{-3}$  and  $2 \times 10^{20} \text{ cm}^{-3}$ , respectively.<sup>35</sup> The same concentration of electrons and holes indicates a band-to-band transfer mechanism, pointing to a typical compensated semi-metal. The Fermi surface of *t*-Hf<sub>2</sub>O<sub>3</sub> is plotted in Fig. 3(c), showing conduction electrons near the Z and  $\Gamma$  points, as well as holes near the R point.

To evaluate the relative stability of this structure, we calculated the molar formation enthalpy of various Hf<sub>2</sub>O<sub>3</sub>, Zr<sub>2</sub>O<sub>3</sub> and Ti<sub>2</sub>O<sub>3</sub> models with respect to their corresponding metals and O<sub>2</sub>. The formation enthalpy of *t*-Hf(Zr)<sub>2</sub>O<sub>3</sub> is -1700 (-1666) kJ/mol, more favorable than fully relaxed corundum Hf(Zr)<sub>2</sub>O<sub>3</sub>, -1586 (-1580) kJ/mol. The chemical transformation from *t*-Hf(Zr)<sub>2</sub>O<sub>3</sub> to *m*-Hf(Zr)O<sub>2</sub> can be written as



and



respectively. On the other hand, the formation enthalpy of fully relaxed Ti<sub>2</sub>O<sub>3</sub> arranged in the  $P\bar{4}m2$  tetragonal structure is -1576 kJ/mol, less favorable than corundum Ti<sub>2</sub>O<sub>3</sub> whose formation enthalpy is -1598 kJ/mol. These results indicate that while the tetragonal  $P\bar{4}m2$  structure is preferred over corundum for Hf(Zr)<sub>2</sub>O<sub>3</sub>, the opposite is true for Ti<sub>2</sub>O<sub>3</sub>.

To our best knowledge, the proposed *t*-Hf<sub>2</sub>O<sub>3</sub> and *t*-Zr<sub>2</sub>O<sub>3</sub> structures have not been reported before, though some experimental data may suggest their existence. Hildebrandt *et al.*<sup>36</sup> performed high-resolution transmission electron microscopy of a conducting HfO<sub>2-x</sub> thin film where the enlarged inverse Fourier-transformed images show a similar structure as in Fig. 3(b). Manory *et al.*<sup>37</sup> discovered two unidentified X-ray diffraction (XRD) peaks at  $2\theta = 40^\circ$  and  $2\theta = 52^\circ$  in

hafnia films grown by ion beam assisted deposition at a transport ratio of 5 and an ion energy of 20 keV. They attributed these peaks to a new tetragonal structure and suggested the  $\text{Hf}_2\text{O}_3$  stoichiometry. However, they simulated their data with a  $P4/mmm$  phase with lattice parameters  $a=5.055 \text{ \AA}$  and  $c=5.111 \text{ \AA}$ , resulting in two small peaks around  $40^\circ$ . We calculated powder XRD patterns<sup>38</sup> for  $t\text{-Hf}_2\text{O}_3$  [Fig. 3(d)] using Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), and found a (110) peak at  $40.7^\circ$  and a (112) peak at  $52.5^\circ$ , close to data. A similar calculation for  $t\text{-Zr}_2\text{O}_3$  yielded a (110) peak at  $40.2^\circ$  and a (112) peak at  $51.6^\circ$ .

In conclusion, we have predicted tetragonal semi-metallic  $\text{Hf}_2\text{O}_3$  and  $\text{Zr}_2\text{O}_3$  structures as the ground state of highly oxygen deficient hafnia and zirconia which undergo a monoclinic-to-tetragonal phase transition. Their semi-metallic properties are characterized by an overlap of the valence band maximum and conduction band minimum at different points of the Brillouin zone, and by low densities of conduction electrons and holes. The presence of  $t\text{-Hf}_2\text{O}_3$  in O-deficient electroformed  $\text{HfO}_x$  is a possible explanation to the conductive state of hafnium-based RRAM.

We specially thank Dr. Blanka Magyari-Köpe from Stanford University for pointing out the experimental results in Ref. 37. This work is financially supported by the Nanosciences Foundation of Grenoble (France) in the frame of the Chairs of Excellence awarded to L.R.C. Fonseca in 2008 and to Y. Nishi in 2010. LRFCF also acknowledges CNPq for financial support. The calculations were performed on the Stanford NNIN (National Nanotechnology Infrastructure Network) Computing Facility funded by the National Science Foundation of USA.

- [1] S. Lange, V. Kiisk, V. Reedo, M. Kirm, J. Aarik, and I. Sildos, *Opt. Mater.* **28**, 1238 (2006).
- [2] J. A. Kilner, *Nat. Mater.* **7**, 838 (2008).
- [3] J. Robertson, *Rep. Prog. Phys.* **69**, 327 (2006).
- [4] A. Asamitsu, Y. Tomioka, H. Kuwahara, and Y. Tokura, *Nature* **388**, 50 (1997).
- [5] S. Q. Liu, N. J. Wu, and A. Ignatiev, *Appl. Phys. Lett.* **76**, 2749 (2000).
- [6] R. Waser and M. Aono, *Nat. Mater.* **6**, 833 (2007).
- [7] B. Magyari-Köpe, M. Tendulkar, S.-G. Park, H. D. Lee, and Y. Nishi, *Nanotechnology* **22**, 254029 (2011).
- [8] D.-H. Kwon, K. M. Kim, J. H. Jang, J. M. Jeon, M. H. Lee, G. H. Kim, X.-S. Li, G.-S. Park, B. Lee, S. Han, M. Kim, and C. S. Hwang, *Nat. Nanotechnol.* **5**, 148 (2010).
- [9] K.-L. Lin, T.-H. Hou, J. Shieh, J.-H. Lin, C.-T. Chou, and Y.-J. Lee, *J. Appl. Phys.* **109**, 084104 (2011).

- [10] K. Kamiya, M. Y. Yang, S.-G. Park, B. Magyari-Köpe, Y. Nishi, M. Niwa, and K. Shiraishi, *Appl. Phys. Lett.* **100**, 073502 (2012).
- [11] P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964); W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- [12] G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996); *Phys. Rev. B* **54**, 11169 (1996).
- [13] P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994); G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- [14] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [15] H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- [16] M. S. Hybertsen and S. G. Louie, *Phys. Rev. B* **30**, 5777 (1984).
- [17] P. Broqvist, A. Alkauskas, and A. Pasquarello, *Phys. Rev. B* **78**, 075203 (2008).
- [18] L. Hedin, *Phys. Rev.* **139**, A796 (1965).
- [19] F. Bruneval, N. Vast, and L. Reining, *Phys. Rev. B* **74**, 045102 (2006).
- [20] The DFT/GGA band structures obtained with the VASP and ABINIT codes differ by less than 10 meV, justifying the application of ABINIT  $G_0W_0$  energy shifts to the VASP eigenvalues.
- [21] N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).
- [22] R. W. Godby and R. J. Needs, *Phys. Rev. Lett.* **62**, 1169 (1989).
- [23] R. E. Hann, P. R. Suitch, and J. L. Pentecost, *J. Am. Ceram. Soc.* **68**, C-285 (1985).
- [24] L. Wang, T. Maxisch, and G. Ceder, *Phys. Rev. B* **73**, 195107 (2006).
- [25] J. G. Speight, *Lange's Handbook of Chemistry*, 16th ed., McGraw-Hill, New York, USA (2004).
- [26] J. X. Zheng, G. Ceder, T. Maxisch, W. K. Chim, and W. K. Choi, *Phys. Rev. B* **75**, 104112 (2007).
- [27] A. S. Foster, V. B. Sulimov, F. L. Gejo, A. L. Shluger, and R. M. Nieminen, *Phys. Rev. B* **64**, 224108 (2001).
- [28] A. S. Foster, F. L. Gejo, A. L. Shluger, and R. M. Nieminen, *Phys. Rev. B* **65**, 174117 (2002).
- [29] N. V. Nguyen, A. V. Davydov, D. Chandler-Horowitz, and M. M. Frank, *Appl. Phys. Lett.* **87**, 192903 (2005).
- [30] M. Houssa, M. Tuominen, M. Naili, V. Afanas'ev, A. Stesmans, S. Haukka, and M. M. Heyns, *J. Appl. Phys.* **87**, 8615 (2000).
- [31] C. Cagli, J. Buckley, V. Jousseau, T. Cabout, A. Salaun, H. Grampeix, J. F. Nodin, H. Feldis, A. Persico, J. Cluzel, P. Lorenzi, L. Massari, R. Rao, F. Irrera, F. Aussenac, C. Carabasse, M. Coue, P. Calka, E. Martinez, L. Perniola, P. Blaise, Z. Fang, Y. H. Yu, G. Ghibaudo, D. Deleruyelle, M. Bocquet, C. Müller, A. Padovani, O. Pirrotta, L. Vandelli, L. Larcher, G. Reimbold, and B. de Salvo,

- IEEE IEDM Tech. Dig., 658 (2011).
- [32] Structures drawn by VESTA: K. Momma and F. Izumi, J. Appl. Crystallogr. **44**, 1272 (2011); Fermi surface drawn by XCrySDen: A. Kokalj, Comput. Mater. Sci. **28**, 155 (2003).
- [33] M. I. Aroyo, J. M. Perez-Mato, C. Capillas, E. Kroumova, S. Ivantchev, G. Madariaga, A. Kirov and H. Wondratschek, Z. Kristallogr. **221**, 15 (2006).
- [34] <http://www.cryst.ehu.es/cgi-bin/cryst/programs/nph-wp-list?gnum=115>.
- [35] N. W. Ashcroft and N. D. Mermin, Solid State Physics, Saunders College Publishing, Philadelphia, PA, USA (1976).
- [36] E. Hildebrandt, J. Kurian, M. M. Müller, T. Schroeder, H.-J. Kleebe, and L. Alff, Appl. Phys. Lett. **99**, 112902 (2011).
- [37] R. R. Manory, T. Mori, I. Shimizu, S. Miyake, and G. Kimmel, J. Vac. Sci. Technol. A **20**, 549 (2002).
- [38] J. Rodríguez-Carvajal, Physica B **192**, 55 (1993).