Structural properties and Thermodynamics of Hafnium sub-oxides in RRAM

Philippe Blaise1,2, a) and Boubacar Traore1,2,3
1) Univ. Grenoble Alpes, F-38000 Grenoble, France.
2) CEA, LETI, MINATEC Campus, F-38054 Grenoble, France.
3) Fondation Nanoscience, 25 rue des Martyrs, 38000 Grenoble, France

(Dated: 25 November 2015)

We study the structural and electronic properties of various hafnium sub-oxides Hf_xO_y from z = 9 to z = 0.5, by ab initio simulation using Density Functional Theory. The stability of these sub-oxides is studied against monoclinic HfO_2. The progressive oxidation of a given Hf_xO_y is also envisaged toward stoichiometric HfO_2.

The analogy with a conductive region of electrons inside a HfO_2 dielectric that leads to the formation of sub-oxides which we denote HfO_x is also envisaged toward stoichiometric HfO_2. Among the different emerging technologies, RRAM based on a metal oxide or OxRRAM5–7 are one of the best candidates to pursue the non volatile memory scaling. Generally speaking an OxRRAM made with HfO_2, (directly compatible with CMOS integration), shows a quasi reversible switching between a low and a high resistance state due to the resistance modulation of a conductive filament of nanometric size7,8. The existence of this filament, which has never been directly identified, is mainly supported by electrical measurements and modeling8,9. As far as the filament hypothesis seems to be relevant, all these models share the hypothesis that is based on oxygen movements between one of the electrodes and the dielectric that leads to the formation of sub-oxides which we denote HfO_x or Hf_xO_y inside the host oxide. Nevertheless Hafnium sub-oxides are not well characterized except for the hafnium-rich compounds of type Hf_xO_y with z ≥ 2, where the sub-lattice spanned by hafnium atoms retains its original hexagonal structure up to the oxygen solubility limit in pure hcp-Hf10. More recently, a semi-metal with a tetragonal Hf_2O_3 structure has been predicted by ab initio simulation11. Moreover, a cousin zirconium-oxide of the hexagonal form ZrO has been predicted as even more stable than the tetragonal Zr_2O_312.

Therefore, we propose ourselves to study by ab initio methods the known hafnium sub-oxides and recently predicted forms. Our simulation results will be useful in order to sustain the filament hypothesis for OxRRAM technology and the related physical characterization experiments.

Our ab initio calculations are performed using Siesta13,14 which implements a generalized gradient approximation (GGA) of density functional theory (DFT)15 thanks to the Perdew-Burke-Ernzerhof (PBE)16 parametrization. Siesta employs a linear combination of numerical atomic orbitals as the basis set to describe the wave functions14. A double zeta plus polarization (DZP) basis set with an energy shift of 50 meV is used in all our calculations. Troullier-Martins pseudopotentials17 were derived with the configurations O 2s^22p^3 and Hf 5d^66s^2, including a non-linear core correction and a relativistic correction for Hafnium. The structural parameters and atomic positions were optimized using a conjugate gradient scheme, until the maximum residual forces and stresses were less than 0.02 eV/A and 200 MPa, respectively. To obtain realistic values for the band gap energy, we employed the half-occupation ab initio technique GGA-1/218 to correct for the self-energy of the oxygen anion. This technique is convenient for extended systems producing band gaps which are in good agreement with experiment and other band gap correction schemes at a negligible extra computational effort19.

The different Hf_xO_y oxides formula we used are summarized in table I with their respective space groups and symmetries. Hafnium metal is known to be hexagonal and presents an unusual high oxygen solubility of 28%. This high solubility is due to the insertion of oxygen atoms inside the octahedral interstices all along specific planes accompanied by a moderate expansion of the c axis of Hafnium. This allows it to retain the hexagonal symmetry down to z = 2. For z = 1 ie. HfO(a), we employed the hexagonal h-ZrO structure proposed by Puchala12 while for HfO_3 we used the tetragonal structure obtained by Xue11. In order to reach the full stoichiometry of HfO_2, we used several other structures: HfO(b) which is obtained by removing an oxygen atom from t-HfO_3, HfO_27(a) obtained by inserting a supplementary oxygen inside t-HfO_3, HfO_2(b) by removing an oxygen atom from a monoclinic supercell of HfO_2 and Hf_32O_63 which is a neutral oxygen vacancy inside a 2x2x2

\[ HfO(a) \]

\[ HfO(b) \]

\[ HfO_27(a) \]

\[ HfO_2(b) \]

\[ Hf_32O_63 \]

---

a) Electronic mail: philippe.blaise@cea.fr
b) Electronic mail: traorehade@yahoo.fr
supercell of monoclinic HfO$_2$. These last structures are not unique but representative of the numerous possibilities that we can expect from these intermediate compositions, (see the discussion below).

| Formula | Space Group | Symmetry | Ref. |
|---------|-------------|----------|------|
| HfO    | P6$_3$/mmc (#194) | Hexagonal | 20 |
| HfO$_6$ | P3 (#147) | Hexagonal | 10 |
| Hf$_2$O | R3 (#148) | Hexagonal | 10 |
| Hf$_3$O | P31 (#147) | Hexagonal | 10 |
| Hf$_4$O | P31m (#162) | Hexagonal | 10 |
| HfO(a) | P62m (#189) | Hexagonal | 12 |
| HfO(b) | P4mm (#129) | Tetragonal | 11 |
| Hf$_2$O$_3$ | P4m2 (#115) | Tetragonal | 11 |
| Hf$_4$O$_2$ (a) | P42m (#111) | Tetragonal | 11 |
| Hf$_4$O$_2$ (b) | P2$_1$/c (#14) | Monoclinic | 11 |
| Hf$_4$O$_6$ | P2$_1$/c (#14) | Monoclinic | 11 |
| HfO$_2$ | P2$_1$/c (#14) | Monoclinic | 21 |

TABLE I. Hf$_2$O crystal structures employed with their respective symmetries and space groups.

All along the path of oxidation of Hafnium it is essential for our study to extract the essential characteristics of the Hf$_2$O sub-oxides. In table II we give the results we obtained in DFT/GGA for: volume of formula unit per Hf atom, its relative increase from the initial hexagonal Hafnium configuration, the mean coordination numbers of Hafnium and Oxygen atoms, the mean bond lengths of Hf–Hf and Hf–O bonds. Then in table III we give: the formation enthalpies per mole of oxygen obtained in GGA (see Eq. 1), the electronic band gap estimated with the half-occupation technique in GGA-1/2 and the mean Bader charges for Hf and O atoms.

As can be seen in tables I and II, below $z = 2$ the phase change from hexagonal to tetragonal to monoclinic symmetries is accompanied by a large volume increase due to oxygen insertion. At the same time, the O coordination number drops from 6 in octahedral position related to the high oxygen solubility in Hf to 3 and 4 for monoclinic HfO$_2$. During this volume increase from hexagonal to monoclinic, Hf–Hf bond lengths are stretched from 3.2 to 3.5 Å while O–Hf bond lengths are kept almost constant at 2.2–2.3 Å.

The formation enthalpies are estimated at T=0 K and P=0 Bar by using the hexagonal Hafnium metal and molecular oxygen as reference states. This corresponds to the following formula where temperature and pressure effects are usually neglected for solid states allowing us to use directly the internal energies we obtained in GGA:

$$\Delta H_f (\text{Hf}_2 \text{O}) = E_{tot} (\text{Hf}_2 \text{O}) - z. E_{tot} (\text{hcp-Hf}) - \frac{1}{2} E_{tot} (\text{O}_2)$$

Eq. 1 corresponds to the formation enthalpy per mole of oxygen employed to create an Hf$_2$O alloy. This formulation permits to gauge enthalpies of sub-oxides with

| Formula | $\Delta H$ (kJ/mol) | $E_g$ (eV) | $Q_{Hf}$ | $Q_{O}$ |
|---------|----------------------|------------|---------|---------|
| HfO     | -561                 | 0.0        | 0.0     | 0.0     |
| Hf$_2$O | -566                 | 0.0        | 0.3     | -1.8    |
| Hf$_4$O | -552                 | 0.0        | 0.5     | -1.8    |
| Hf$_4$O | -546                 | 0.0        | 0.6     | -1.8    |
| Hf$_2$O | -532                 | 0.0        | 0.9     | -1.8    |
| HfO(a)  | -521                 | 0.4        | 1.6     | -1.6    |
| HfO(b)  | -498                 | 0.0        | 1.5     | -1.5    |
| Hf$_2$O$_3$ | -513            | 0.0        | 2.2     | -1.5    |
| Hf$_4$O$_2$ (a) | -491          | 0.4        | 2.4     | -1.4    |
| Hf$_4$O$_2$ (b) | -500          | 1.1        | 2.4     | -1.4    |
| Hf$_4$O$_6$ | -513            | 5.8        | 2.7     | -1.4    |
| HfO$_2$ | -515                 | 5.8        | 2.7     | -1.4    |

TABLE III. Hf$_2$O physical properties: formation enthalpy in kJ/mol of oxygen obtained in GGA, estimated band gap in eV (GGA-1/2), mean Bader charge for Hf and O in $|e|$. 

$\%_{inc.}$ and $\#Hf$ and $\#O$ are the percentage increase of volume and number of Hf and O atoms respectively calculated from initial hexagonal HfO$_2$ structure.

TABLE II. Hf$_2$O structural properties: volume in $\lambda^3$ per Hafnium atom with experimental values inside parentheses, relative volume increase in % per Hf atom, $\#$ of Hf and O first neighbors, mean atomic distance of Hf–Hf and O–Hf bonds in $\lambda$. 

$\%_{inc.}$ is the relative volume increase in % per Hf atom and $\#$ of Hf and O first neighbors, mean atomic distance of Hf–Hf and O–Hf bonds in $\lambda$. 

$\%_{inc.}$ and $\#Hf$ and $\#O$ are the percentage increase of volume and number of Hf and O atoms respectively calculated from initial hexagonal HfO$_2$ structure.
different stoichiometries with the help of Tab. III. By comparing with the experimental value of $\Delta H = -1144.7$ kJ/mol of HfO$_2$, we recover the well known underbinding effect due to partial cancellation of errors in GGA: $-1144.7/2 = -572$ kJ/mol of oxygen (exp.) vs -515 kJ/mol (GGA).

We now turn to the basic electronic properties of the sub-oxides. Table II and III show that the mean Bader charge increase for Hf atoms is directly correlated to the Hf$_2$O volume increase, to a lower number of first neighbor oxygen atoms and to the band gap opening. For the electronic band gap the situation seems however to be more complex: the original bang gap of m-HfO$_2$ at 5.8 eV is preserved only for a small concentration of oxygen vacancies (at a few %) but drops considerably to 0.4 eV for Hf$_2$O$_7$(a) and becomes null for Hf$_2$O$_3$ which is a semi-metal$^{11}$. Then it increases again at 0.4 eV for hexagonal HfO(a) to vanish completely for the remaining compositions at $x \geq 2$. This seems to be partially related to the Hf–Hf bond length which has to be sufficiently large and $\geq 3.4$ Å to insure some insulating properties. For HfO(a) we also do believe that the rather specific HfO hexagonal symmetry is at the origin of its slight gap increase. Note that this mixture of (semi-)metallic and semiconductor characteristics could also be probably related to the resistance variability in OxRRAM studies$^{22}$.

These calculated data constitute a starting point to describe the essential thermodynamics of HfO$_2$-based OxRRAM. In OxRRAM technology a forming step is usually required to render the initially insulating HfO$_2$ conductive, allowing electrons to flow through a Hafnium-rich conductive path or filament$^{23}$. By neglecting the interface effects (i.e. for a sufficiently large filament), we can envisage the stability of a pure Hf filament in equilibrium with HfO$_2$ against oxidation by considering the following reaction:

$$\text{Hf} + \frac{x}{2-x}\cdot\text{HfO}_2 \rightarrow \frac{2}{2-x}\cdot\text{HfO}_x \quad 0 \leq x < 2 \quad (2)$$

The basic idea behind equilibrium Eq. 2 is to consider the pure Hafnium filament as a limit of an Hf-alloy with oxygen atoms shared with the surrounding HfO$_2$. The corresponding enthalpy curve for equilibrium Eq. 2 is shown in Fig. 1. At $x = 0$ the pure Hf limit serves as a reference energy $\Delta H = 0$, indicating that the O chemical potential is assumed to be the one in an Hf-rich environment. Therefore, for $x \rightarrow 2$ the corresponding enthalpy tends exactly toward two times the formation enthalpy of an oxygen vacancy in the Hafnium-rich limit. In between, there exists a stability interval for sub-oxides enriched in oxygen from $x \approx 0.2$ up to $x \approx 1$. This tells that after forming, an Hf-rich region in contact with HfO$_2$ tends to form an HfO$_2$ composition, with $x$ around 0.5 or Hf$_2$O. This is in relative agreement with the results of McKenna$^{24}$ who proposed Hf$_2$O as the most stable composition by following a different thinking, because here we consider several new structures for the Hafnium sub-oxides with notably $x = 1$.

![FIG. 1. HfO$_x$ stability against pure Hf and HfO$_2$ in infinite proportion. The black curve is derived using eq. 2 and table III. For $x = 1$ the upper point is for HfO(b) structure. For $x$ close to 2 we also show the energy obtained using data from.$^{25}$](image)

Thereafter the forming step, starting from a given composition of the filament we may wonder about the energetic of oxidation. The following equilibrium

$$\text{Ti}_n\cdot\text{O}_i + \frac{1}{2x-1}\cdot\text{Hf}_x\text{O} \rightarrow \text{Ti}_n + \frac{z}{2x-1}\cdot\text{HfO}_x \quad 0 \leq x \leq 2 \quad (3)$$

allows us to investigate the oxidation of a filament of Hf$_2$O composition by oxygen interstitial atoms coming from a reactive electrode made of titanium in contact with the formed dielectric$^{26}$. The Ti$_n$O$_i$ and Ti$_n$ systems have been calculated in GGA starting from a relaxed hcp-Ti structure made of 150 atoms with one oxygen inserted in octahedral position. The obtained results for several starting compositions of Hf$_x$O namely Hf, Hf$_2$O, Hf$_3$O and HfO are shown in Fig. 2. For pure Hf and, to a lesser extent, Hf$_6$O we obtain that these compositions are stabilized toward Hf$_2$O and Hf$_3$O respectively, which definitely favors sub-oxide filaments to be stable in contact with both m-HfO$_2$ and hcp-Ti. Then, the increase of the oxygen content of a Hafnium sub-oxide in contact with Ti requires a near constant energy of 0.2 eV per oxygen atom added. The only exception occurs for the Hf$_5$O$_7$ composition which requires 0.3 eV up to 0.6 eV. Interestingly, if one follows the forbidden gap increase related to oxygen content as shown in the lower part of Fig. 2, this slight increase delimits exactly the conductive compositions from the insulating one. Therefore, we can argue that resetting an OxRRAM made of HfO$_2$ (i.e programming the device in a high resistance state) is mainly related to a bio-stable behavior of the oxidation of Hf$_x$O which can be oxidized partly as a conductor and partly as an insulator. Depending on the kinetic conditions which we do not treat here, one can imagine that the insulator fraction due to partial oxidation of a sub-oxide filament
can vary a lot in position and shape leading to the intrinsic variability of the high resistive state \( R_{\text{off}} \) observed experimentally for this type of OxRRAM\(^{22,27}\).

![Graph](image-url)

**FIG. 2.** \( \text{Hf}_2\text{O} \) oxidation enthalpy by oxygen atoms coming from a hcp-Ti electrode up to \( \text{HfO}_2 \), for various starting compositions \( z = \infty, 6, 3, 1 \). The lower part shows the associated forbidden band gap.

In conclusion, with the help of simulations based on density functional theory, we derived the basic properties of the most stable Hafnium sub-oxides. This allowed us to find the most stable compositions of sub-oxides in equilibrium with \( \text{HfO}_2 \) relative to the forming step of RRAM, but also the most stable compositions of sub-oxides in equilibrium with a reactive Titanium electrode during the RESET step. Our equilibrium calculations come from standard thermodynamics and neglect several important effects like the kinetic effects, the interface effects, which are all relevant at a nanometric scale. Nevertheless, as a first order approach, our results reveal face effects, which are all relevant at a nanometric scale.

The authors thank the Nanoscience Foundation of Grenoble (France) for its financial support.

---

1G. D. Wilk, R. M. Wallace, and J. M. Anthony, Journal of Applied Physics 89, 5243 (2001).
2K. Mistry, C. Allen, C. Auth, B. Beattie, D. Bergstrom, M. Bost, M. Brazier, M. Buehler, A. Cappellani, R. Chau, C.-H. Choi, G. Ding, K. Fischer, T. Ghanil, R. Grover, W. Han, D. Hansen, M. Hattendorf, J. He, J. Hicks, R. Huessner, D. Ingerly, P. Jain, R. James, L. Jong, S. Joshi, C. Kenyon, K. Kuhn, K. Lee, H. Liu, J. Maiba, B. McIntyre, P. Moon, J. Neirynck, S. Pae, C. Parker, D. Parsons, C. Prasad, L. Pipes, M. Prince, P. Ranade, T. Reynolds, J. Sandford, L. Shifren, J. Sebastian, J. Seiple, D. Simon, S. Sivakumar, P. Smith, C. Thomas, T. Troeger, P. Vandervoor, S. Williams, and K. Zawadzki, in Electron Devices Meeting, 2007. IEDM 2007. IEEE International (2007) pp. 247–250.
3P. McIntyre, ECS Transactions 11, 235 (2007), http://www.ecst.esd.org/content/11/4/235.full.pdf+html.
4S. Jeong, R. Thomas, R. S. Katiyar, J. F. Scott, H. Kohlstedt, A. Petraru, and C. S. Hwang, Reports on Progress in Physics 75, 076502 (2012).
5A. Beck, J. G. Bednorz, C. Gerber, C. Rossel, and D. Widmer, Applied Physics Letters 77, 139 (2000).
6L. Baek, M. Lee, S. Seo, M.-J. Lee, D. Seo, D.-S. Suh, J. Park, S. Park, T. Kim, I. Yoo, U.-i. Chung, and J. Moon, in Electron Devices Meeting, 2004. IEDM Technical Digest. IEEE International (2004) pp. 587–590.
7H.-S. Wong, H.-Y. Lee, S. Yu, Y.-S. Chen, Y. Wu, P.-S. Chen, B. Lee, F. Chen, and M.-J. Tsai, Proceedings of the IEEE 100, 1951 (2012).
8G. Bersuker, D. C. Gilmer, D. Vekslar, P. Kirsch, L. Vandelli, A. Padovani, L. Larcher, K. McKenna, A. Shluger, V. Iglesias, M. Porti, and M. Nafr, Journal of Applied Physics 110, 124518 (2011).
9L. M. Prcel, L. Trojman, J. Moreno, F. Crupi, V. Maccarino, R. Degraeve, L. Goux, and E. Simoen, Journal of Applied Physics 114, 074509 (2013).
10P. P. Burton and A. van de Walle, Calphad 37, 151 (2012).
11K.-H. Xue, P. Blaise, L. R. C. Fonseca, and Y. Nishi, Phys. Rev. Lett. 110, 065502 (2013).
12B. Puchala and A. Van der Ven, Phys. Rev. B 88, 094108 (2013).
13http://www.icmab.es/dmmis/leem/siesta/.
14J. M. Soler, E. Artacho, J. D. Gale, A. Garca, J. Junquera, P. Ordejnn, and D. Sachez-Portal, Journal of Physics: Condensed Matter 14, 2745 (2002).
15R. G. Parr and W. Yang, Density-Functional Theory of Atoms and Molecules (New York: Oxford University Press, 1982).
16P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
17N. Troullier and J. L. Martins, Phys. Rev. B 43, 1993 (1991).
18L. G. Ferreira, M. Marques, and L. K. Teles, Phys. Rev. B 78, 125116 (2008).
19L. M. Ribeiro, L. R. C. Fonseca, and L. G. Ferreira, Phys. Rev. B 79, 241312 (2009).
20R. B. Russell, Journal of Applied Physics 24, 232 (1953).
21J. E. Lowther, J. K. Dewhurst, J. M. Leger, and J. Haines, Phys. Rev. B 60, 14485 (1999).
22A. Fantini, L. Goux, R. Degraeve, D. Wouters, N. Raghavan, G. Kar, A. Belmonte, Y.-Y. Chen, B. Govoreau, and M. Jurzak, in Memory Workshop (IMW), 2013 5th IEEE International (2013) pp. 30–33.
23K.-H. Xue, B. Traore, P. Blaise, L. Fonseca, E. Vianello, G. Molas, B. De Salvo, G. Ghibaudo, B. Magyari-Kope, and Y. Nishi, Electron Devices, IEEE Transactions on 61, 1394 (2014).
24K. P. McKenna, Modelling and Simulation in Materials Science and Engineering 22, 025001 (2014).
25J. X. Zheng, G. Ceder, T. Maxisch, W. K. Chim, and W. K. Choi, Phys. Rev. B 75, 104112 (2007).
26Y.-S. Chen, H.-Y. Lee, P.-S. Chen, T.-Y. Wu, C.-C. Wang, P.-J. Tseng, F. Chen, M.-J. Tsai, and C. Lien, Electron Device Letters, IEEE 31, 1473 (2010).
27T. Cabout, L. Perniola, V. Jousseamine, H. Grampieux, J. Nodin, A. Toffoli, M. Guillermet, E. Jalaguier, E. Vianello, G. Molas, G. Reimbold, B. De Salvo, T. Diokh, P. Candelier, O. Pirrotta, A. Padovani, L. Larcher, M. Bocquet, and C. Muller, in Memory Workshop (IMW), 2013 5th IEEE International (2013) pp. 116–119.