# Oxygen migration around the filament region in HfO<sub>x</sub> memristors

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# ABSTRACT

The exact composition and structure of conductive filaments in hafnia-based memristors are still not fully understood, but recent theoretical investigations reveal that hexagonal  $HfO_x$  phases close to the h.c.p. Hf structure are probable filament candidates. In this work we list h.c.p. Hf,  $Hf_6O$ ,  $Hf_3O$  and  $Hf_2O$  as possible phases for the filament in hafnia memristors. Their differences in lattice parameters, electronic structures and O charge states are studied in details. Migration of O ions for both in-plane and out-of-plane directions in these phases is investigated using first-principles calculations. Both single-phase supercells and filament-in-dielectric models are used for migration barrier calculations, while the latter is proven to be more accurate for the *c*-direction. The migration of O ions is fastest in metal Hf, while slowest in  $Hf_2O$ . The existence of O interstitials in Hf tends to hinder the transport of O.

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# I. INTRODUCTION

Binary oxide-based memristors<sup>1,2</sup> that demonstrate stable resistive switching phenomenon<sup>3,4</sup> are considered as promising candidates for next-generation non-volatile memory in microelectronics. Among them, more attention has been paid to HfO<sub>x</sub>, TaO<sub>x</sub>,  $TiO_x$  and  $AlO_x$ ,<sup>5-15</sup> due to their excellent technical compatibility to CMOS flow-line. When active electrodes such as Ag and Cu are not involved, their resistive switching phenomena belong to the valence change mechanism.<sup>3</sup> In this case the movement of O anions and the formation of oxygen-deficient conductive filaments (CFs) are the common features that account for their resistive switching, but the exact composition of the CF is specific to each memristor material. For example, the Magnéli phase crystal TinO2n-1 has been identified as the CF structure in TiO<sub>x</sub>-based memristors,<sup>16</sup> while for  $TaO_x$  memristors the CF composition was found to be  $TaO_{1-x}$ and probably amorphous.<sup>18</sup> When it comes to  $HfO_x$ , which has been intensively studied as a very promising and reliable memristor material, the exact CF composition is unfortunately less known. Recent experimental investigations agree on the point that the CF in  $HfO_x$  consists of O vacancies, <sup>19–24</sup> but the composition (or composition range) of the CF was not given explicitly. Hence, it is still a challenging task to directly identify the CF composition and structure of  $HfO_x$ -memristors from transmission electron microscopy and scanning tunneling microscopy.<sup>25</sup>

On the other hand, theoretical investigation on the reduction process of HfO<sub>2</sub> may provide useful information about the CF composition in HfO<sub>x</sub> memristors. Although the thermodynamically stable HfO<sub>x</sub> ( $0 \le x \le 2$ ) phases at room temperature only involve monoclinic HfO<sub>2</sub> (m-HfO<sub>2</sub>), hexagonal Hf<sub>6</sub>O and hexagonal Hf,<sup>26</sup> several intermediate phases have been predicted through first-principles calculations.<sup>27-30</sup> Upon reduction, the structure of HfO<sub>x</sub> basically experiences a transition from tetragonal to hexagonal symmetry as shown in Figure 1. While the initial composition HfO<sub>2</sub> points to a monoclinic  $P2_1/c$  phase, it can become tetragonal (a distorted fluorite structure with space group  $P4_2/nmc$ ) when heated up to ~2000 K.<sup>31,32</sup> Except for HfO<sub>2</sub>, the other HfO<sub>x</sub> compositions follow the tetragonal-to-hexagonal trend. For instance,



the ground state of  $Hf_2O_3$  has been predicted to be tetragonal  $P\bar{4}m2$ ,<sup>27</sup> and the ground state of HfO was predicted by Zhu et al. as tetragonal  $I4_1/amd$ .<sup>30</sup> Nevertheless, another hexagonal phase of HfO (h-HfO), following  $P\bar{6}2m$  ZrO,<sup>28</sup> is also close in energy.<sup>29</sup> Subsequently, for HfO<sub>1-x</sub> several trigonal/rhombohedral structures have been known, including Hf<sub>2</sub>O, Hf<sub>3</sub>O and Hf<sub>6</sub>O. These phases can simply be regarded as hexagonal metal Hf with certain amount of O interstitials, thus in this work we categorize them into a global hexagonal HfO<sub>x</sub> class. All these sub-oxide phases with HfO<sub>1.5-x</sub> stoichiometry are metallic or with very tiny band gap (as in the case of h-HfO<sup>29</sup>). Yet, according to the thermodynamic calculation of McKenna,<sup>33</sup> as well as the O vacancy chain cohesion study from Xue et al.,<sup>34</sup> it is reasonable to attribute the CF in HfO<sub>x</sub> memristors to those hexagonal phases close to metal Hf, such as Hf<sub>2</sub>O, Hf<sub>3</sub>O, Hf<sub>6</sub>O and Hf.

Nevertheless, the difference among various hexagonal  $HfO_x$  phases as the CF is still not known. In particular, during the socalled RESET operation, which corresponds to the rupture of the filaments by surrounding O anions as illustrated in Figure 2 (SET is the opposite process to turn the device into low-resistance state), O movement is at the heart of the switching mechanism.<sup>35</sup> On the one hand, the pre-existence of O interstitials in the CF may hinder the further transport of O anions inside the CF. On the other hand, these O interstitials may also expand the volume of the CF to facilitate O anion transport therein. Understanding the special characteristics of various  $HfO_x$  CF candidates is beneficial for experimental identification of the true CF composition and structure. In this work, we focus on the migration of O anion inside or across these CF candidates, and will calculate the various diffusion barriers in these processes, which can afford valuable information on the CF formation and rupture kinetics in HfO<sub>x</sub> memristors.



FIG. 2. Movement of O anions during the RESET process of a typical TiN/HfO<sub>2</sub>/Pt memristor cell.

Hf

Hf<sub>6</sub>O

Hf<sub>3</sub>O

Hf<sub>2</sub>O

HfO

of the supercells containing 18 Hf atoms.							
Composition	Optimized lattice parameters						
	a (Å)	a' (Å)	c (Å)	c' (Å)			
	d (A)	a (A)	C (A)	ι			

5.527

5.545

5.571

5.562

5.226

5.069

15.336

15.355

5.148

3.172

15.207

15.336

15.355

15.445

19.035

**TABLE I.** Lattice parameters of various  $HfO_x$  phases in the hexagonal class, obtained with GGA-PBE calculations. The effective parameters a' and c' correspond to those of the supercells containing 18 H atoms

### **II. COMPUTATIONAL METHOD**

3.191

5.545

5.571

5.562

5.226

We carried out density functional theory calculations using the plane-wave basis set and the projector augmented-wave method, as implemented in the Vienna *Ab initio* Simulation Package (VASP).<sup>36,37</sup> A constant 500 eV plane-wave kinetic energy cutoff was used throughout the calculations. For exchange-correlation energy, the generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE) was utilized.<sup>38</sup> The valence electron configurations are 5d and 6s for Hf, as well as 2s and 2p for O. The Brillouin zones were sampled using  $\Gamma$ -centered kpoint mesh. For Hf<sub>x</sub>O supercells, a 5×5×3 mesh was used, while only the  $\Gamma$  point was used for filament-in-dielectric models. Diffusion barriers were calculated using a climbing image nudged elastic band (CI-NEB) method, developed by Henkelman and H. Jónsson.<sup>39</sup>

# **III. RESULTS AND DISCUSSIONS**

In Table I we list the optimized lattice constants of h.c.p. Hf,  $h-Hf_6O$ ,  $h-Hf_3O$ ,  $h-Hf_2O$  and h-HfO. As their unit cells contain

different numbers of Hf atoms, we here define a set of effective lattice parameters a' and c' for better comparison. These parameters are based on the unit cell of h-Hf<sub>6</sub>O, which has 18 Hf atoms in total. Hence, in other materials a' and c' are the supercell lattice parameters, such that the supercell also contains 18 Hf atoms. As illustrated in Figure 3, both a' and c' increase monotonously from Hf to Hf<sub>3</sub>O. After adding more O interstitials to reach the Hf<sub>2</sub>O stoichiometry, however, only c' increases, rather than a', but the variations are so tiny that Hf<sub>2</sub>O may still be categorized into the same class as Hf<sub>6</sub>O and Hf<sub>3</sub>O, as they are all based on h.c.p. Hf. The *P*62*m* phase of h-HfO is, however, topologically quite different from the other phases as shown in Figure 1. Consequently, it demonstrates a great shrink in the a' value, but in the mean time a very large expansion along the c-direction.

An investigation into the electronic structures shows that  $Hf_6O$ ,  $Hf_3O$  and  $Hf_2O$  possess similar density of states (DOS) around the Fermi level as metal Hf, and all phases are good conductors (see Figure 4). However, the bandwidth of the O sub-band strongly depends on the stoichiometry. A very narrow O sub-band emerges slightly below -7 eV (with respect to the Fermi level, *sic passim*) in  $Hf_6O$ , which is broadened substantially in  $Hf_3O$ . Moreover, in  $Hf_3O$  the upper O sub-band edge moves to around -6.5 eV. For  $Hf_2O$ , the O sub-band becomes even broader, whose upper edge further increases a bit. The trend is reasonable since ultimately in  $HfO_2$ , the valence band maximum will be dominated by states from O, rather than  $Hf_4^{40}$ 

Subsequently, we focus on the charge state of the O atoms in these  $HfO_x$  phases. To this end we calculated their Bader charges in the primitive cells. As summarized in Table II, in all phases O atoms are in perfect -2 valency, i.e.,  $O^{2-}$  anions. Hence, it is in general not possible to achieve neutral O atoms inside the CF of hafnia-based memristors. The charge status of O has been fixed by the Hf environment, which is very similar to a recent finding that the Ag charge status is determined by some solid-state electrolyte environments.<sup>41</sup> To further strengthen this point, we have set up HfO<sub>x</sub> supercells



FIG. 3. Variation of the effective lattice parameters upon inserting O interstitials into metal Hf: (a) a-axis; (b) c-axis. The stoichiometries here cover Hf, Hf<sub>6</sub>O, Hf<sub>3</sub>O, Hf<sub>2</sub>O and HfO.



FIG. 4. (a) Electronic density of states (DOS) of h.c.p. metal Hf; (b) DOS and partial DOS of Hf<sub>6</sub>O; (c) DOS and partial DOS of Hf<sub>3</sub>O; (d) DOS and partial DOS of Hf<sub>2</sub>O.

**TABLE II.** List of calculated O Bader charges inside various  $HfO_x$  phases. In the primitive cell calculation, the values refer to the O atoms in the perfect stoichiometry. For supercell calculations, the values refers to that of an extra O interstitial introduced, either neutral or with two extra electrons (the "2e" case).

	Number of charges on O according to the Bader gauge				
	Primitive cell		Interstitial in supercell		
Composition	O-I	O-II	Neutral	2e	
Hf	-	-	-2.10	-2.10	
Hf <sub>6</sub> O	-2.09	-	-2.06	-2.06	
Hf <sub>3</sub> O	-2.09	-	-2.03	-1.99	
Hf <sub>2</sub> O	-2.04	-2.06	-1.96	-1.96	

AIP Advances 9, 105007 (2019); doi: 10.1063/1.5122989 © Author(s) 2019 (with at least 72 atoms), and introduce an extra O interstitial, either in the neutral O atom form, or in the  $O^{2-}$  anion form. The following Bader charge calculation confirms that there is almost no difference on the charge status of this extra O interstitial (Table II). Note that there is only one kind of O site in Hf<sub>6</sub>O and Hf<sub>3</sub>O, but two in the case of Hf<sub>2</sub>O. The site named O-I is in the sparse interval layer that contains less O atoms, while the site named O-II is in the dense interval layer of Hf<sub>2</sub>O.

After identifying the delicate differences among the fundamental properties of these CF candidates, we then calculate the O anion migration barriers within these phases. Since the fundamental properties of h-HfO deviate from the Hf—Hf<sub>6</sub>O—Hf<sub>3</sub>O—Hf<sub>2</sub>O series, such as in the trend of lattice constant, we here focus only on Hf, Hf<sub>6</sub>O, Hf<sub>3</sub>O and Hf<sub>2</sub>O. For each phase, a supercell of around 1 nm × 1 nm × 1.5 nm was set up to carry out NEB calculations. The migration paths are illustrated in Figure 5, and the migration barriers are listed in Table III as well as illustrated in Figure 6. Two



FIG. 5. Migration paths under investigation for (a) O interstitial inside Hf; (b) O inside Hf<sub>6</sub>O; (c) O interstitial inside Hf<sub>6</sub>O; (d) O inside Hf<sub>3</sub>O; (e) O interstitial inside Hf<sub>3</sub>O; (f) O inside Hf<sub>2</sub>O. The starting points of the paths are marked by red arrows.

<b>TABLE III.</b> List of migration energy barriers of O ions inside Hf, Hf <sub>6</sub> O, Hf <sub>3</sub> O and Hf <sub>2</sub> O,	
calculated using supercells with fixed dimension.	

	Migration barriers				
	Along <i>a-b</i>	Along <i>b</i>	Vertical (along <i>c</i> )		
	Hf				
O (Interstitial)	1.99 eV	1.97 eV	3.12 eV		
	Hf <sub>6</sub> O				
O (Original)	2.27 eV	2.26 eV	3.47 eV		
O (Interstitial)	2.06 eV	2.05 eV	3.05 eV		
	Hf <sub>3</sub> O				
O (Original)	2.37 eV	2.36 eV	3.33 eV		
O (Interstitial)	2.50 eV	1.96 eV	2.85 eV		
	Hf <sub>2</sub> O				
O (Original)	2.50 eV	2.51 eV	3.64 eV		

trends are clearly observed. First, the in-plane migration barriers (*a-b* or *b* direction) are enlarged when more O are intercalated into the Hf lattice. Take the *b*-direction as an example. The migration barrier follows the sequence of Hf (1.97 eV) < Hf<sub>6</sub>O (2.26 eV) < Hf<sub>3</sub>O (2.36 eV) < Hf<sub>2</sub>O (2.51 eV). This implies that the pre-existing O atoms inside Hf tend to hinder the in-plane O migration, whose effect overwhelms the lattice constant expansion. Secondly, the vertical migration barriers along *c*-axis are generally much larger than the corresponding in-plane migration barriers. We also find that in most cases, as an extra O interstitial, the migration barriers get lowered compared with moving an existing O atom in these CF candidates.

One should, however, be cautious about the migration barrier results calculated using fixed supercells, since the imposed geometry constraints can be too strong to imitate the experimental situation. To further estimate the accuracy of our migration barriers, we studied the transport of O ions in "filament-in-dielectric" models that seem more practical from an experimental point of view. For Hf-in-HfO<sub>2</sub> model (417 atoms), we established a partial CF structure such that the migration barriers both in the lateral direction and in the vertical direction can be calculated (Figure 7 a-b). A more complicated Hf<sub>6</sub>O-in-HfO<sub>2</sub> model with 526 atoms was also set up as in Figure 7 c-d, where the CF is continuous due to the large lateral area and size limitation. To cover more possibilities of migration, for some barriers we calculated two distinct paths. The lateral migration barrier of an O ion from m-HfO<sub>2</sub> to metal Hf was estimated to be 1.73 eV and 1.86 eV along two different paths (one of them illustrated in Figure 7 a), both very close to the lateral migration barrier inside pure Hf (1.97 eV - 1.99 eV). On the other hand, the vertical entrance into metal Hf suffers from a barrier of 1.79 eV to 1.82 eV (see Figure 7 b), which is substantially lower than that inside metal Hf calculated previously along *c*-axis (3.12 eV, obtained using the supercell approach). To exclude the

influence of interface penetration, we further calculated the migration barrier of this intercalated O ion inside Hf along its *c*-axis, and found only a 1.50 eV migration barrier (less than a half of the value calculated using the supercell approach). In the case of Hf<sub>6</sub>Oin-HfO<sub>2</sub>, the lateral migration barrier was estimated to be 2.04 eV and 2.44 eV following two paths, respectively (one of them illustrated in Figure 7 c). The vertical barrier is 1.82 eV following the path in Figure 7 d, which is also much smaller than that inside pure Hf<sub>6</sub>O (3.05 eV).

A paradox then arises as the migration barriers calculated using supercell approach and filament-in-dielectric approach do not fully agree with each other. While for in-plane barriers they support each other, for vertical migration barriers the supercell approach predicts much higher energy barriers than the values obtained using ultra-large filament-in-dielectric models. It needs to be pointed out here that the latter approach is more accurate, while the supercell approach over-estimated the barriers along *c*-axis, as explained below. The *a-b* plane is a close-pack plane in metal Hf. When O ions migrate along c-axis, they must penetrate these dense atomic planes made of Hf. As the supercell dimensions were fixed during NEB calculations, this is quite difficult since the Hf close-pack plane can hardly show large in-plane deformation. However, in the latter approach, there are Hf/HfO2 interfaces involved, which can be subject to compression more easily. In experiments, a CF is limited in lateral size and its interfaces with the surrounding dielectric can indeed be compressed to allow for vertical O penetration. Therefore, the lower vertical migration barriers, such as the 1.82 eV barrier in Hf<sub>6</sub>O, make more sense than the supercellobtained values (3.47 eV, or 3.05 eV if in the foreign interstitial form). On the other hand, the accurate in-plane migration barriers calculated using the supercell approach can also be understood from the special h.c.p. structure of metal Hf. As the c-direction is perpendicular to the close-pack plane, Hf atomic planes could demonstrate deformation in this direction easily. When O migrates in the gap region between two Hf atomic planes, vertical displacement of adjacent Hf atoms naturally occurs to ensure the transport even in fixed supercell format. After considering the limitation of the fixed supercell approach, we conclude that in these CF candidates the migration of O ions along c-axis is at least as easy as the inplane directions. In any direction, the typical migration barrier is less than 3 eV.

The mechanism discussed above may also be used to explain some over-estimated theoretical migration barriers in the literature. For instance, the diffusion barrier of O in h.c.p. Ti was calculated to be 3.5 eV by Traoré et al. using the supercell approach, which was regarded as too high.<sup>42</sup> It can be more realistic to use a multi-grain model so as to allow for the necessary interfacial deformation.

Our calculation results imply that O migration is possible for both in-plane and out-of-plane directions for h.c.p. Hf-like CFs. Experimental evidences are still lacking regarding whether it is the *c*-axis or the a/b axis of the metal that is perpendicular to the capacitor area. However, in any case our results show that O migration can occur both vertically and horizontally during RESET and SET operations. The vertical movement directly leads to the rupture or re-formation of the CF at its weak location, while the horizontal movement is relevant to the shrink/growth of the CF lateral dimensions.



**FIG. 6.** Energy profiles during the CI-NEB calculations for the transport of (a) O interstitial inside Hf; (b) O inside Hf<sub>6</sub>O; (c) O interstitial inside Hf<sub>6</sub>O; (d) O inside Hf<sub>3</sub>O; (e) O interstitial inside Hf<sub>3</sub>O; (f) O inside Hf<sub>2</sub>O.

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**FIG. 7.** Migration paths for O from the dielectric region to the CF region. (a) Lateral migration from m-HfO<sub>2</sub> to Hf; (b) vertical migration from m-HfO<sub>2</sub> to Hf; (c) lateral migration from m-HfO<sub>2</sub> to Hf<sub>6</sub>O; (d) vertical migration from m-HfO<sub>2</sub> to Hf<sub>6</sub>O.

### **IV. CONCLUSION**

The reduction process of HfO2 generally involves a lattice symmetry transformation from tetragonal to hexagonal, where the transition point lies at HfO. Hence, h.c.p. Hf, Hf<sub>6</sub>O, Hf<sub>3</sub>O and Hf<sub>2</sub>O are potential candidate phases for the conductive filament in HfO2based memristors. Bader charge calculation confirms that the O interstitials in these phases are in perfect O2- anion form, which precludes the possible existence of neutral O atoms inside metal Hf. The difficulty of O ion migration in these phases depends on the concentration of exiting O interstitials. The in-plane migration barrier along b-axis increases from 1.97 eV in the case of Hf, to 2.51 eV in the case of Hf<sub>2</sub>O. Hence, the existing O ions tend to hinder in-plane migration of O, such that pure metal Hf is the fastest media for O transport in the series of filament candidates considered in this work. The vertical migration barriers are over-estimated by the fixed supercell approach, but using larger filament-in-dielectric models we obtained typical migration barriers along c-axis as 1.50 eV and 1.82 eV in Hf and Hf<sub>6</sub>O, respectively. Our calculation supports fast migration of O anions around the Hf/Hf<sub>6</sub>O filaments in HfO<sub>2</sub>-based memristors, regardless of the direction of transport, but adding more O interstitials in the filament tends to hinder the O transport.

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