



## Communication

Surface ferromagnetism in HfO<sub>2</sub> induced by excess oxygenQinfang Zhang<sup>a,b,\*</sup>, Guohong Chen<sup>b,c</sup>, Seiji Yunoki<sup>b,d,e</sup><sup>a</sup> Key Laboratory for Advanced Technology in Environmental Protection of Jiangsu Province, Yancheng Institute of technology, Yancheng 224051, China<sup>b</sup> Computational Condensed Matter Physics Laboratory, RIKEN ASI, Saitama 351-0198, Japan<sup>c</sup> Key Laboratory of Computational Physical Sciences (Ministry of Education) Department of Physics, Fudan University, Shanghai 200433, China<sup>d</sup> Computational Quantum Matter Research Team, RIKEN Center for Emergent Matter Science (CEMS), Wako, Saitama 351-0198, Japan<sup>e</sup> Computational Materials Science Research Team, RIKEN Advanced Institute for Computational Science (AICS), Kobe, Hyogo 650-0047, Japan

## A B S T R A C T

First-principles numerical simulations based on density functional theory are performed to examine surface electronic and magnetic properties of cubic, tetragonal, and monoclinic HfO<sub>2</sub> with low index terminations. Our systematic calculations reveal that i) stoichiometric surfaces and Hf rich non-stoichiometric surfaces are non magnetic, and ii) O rich non-stoichiometric surfaces are ferromagnetic and metallic. The ferromagnetism found here is attributed to O surface electronic states with large O 2*p* spin exchange energy. This finding provides a novel pathway to *d*<sup>0</sup> ferromagnetism for simple oxides with no magnetic ions involved. We also calculate the surface energy and discuss a recent controversial issue of ferromagnetism observed experimentally in HfO<sub>2</sub>.

## 1. Introduction

A lot of effort has been devoted in the field of spintronics to create a new concept and search for a new functionality of spin-driven nano devices for applications to the next generation electronics, where ferromagnetic materials play a central role [1]. Most extensively studied in this direction is a class of dilute magnetic semiconductors for which magnetic impurities are introduced in otherwise non magnetic semiconductors. Many interesting properties such as a possible room temperature ferromagnetism have been already reported [2].

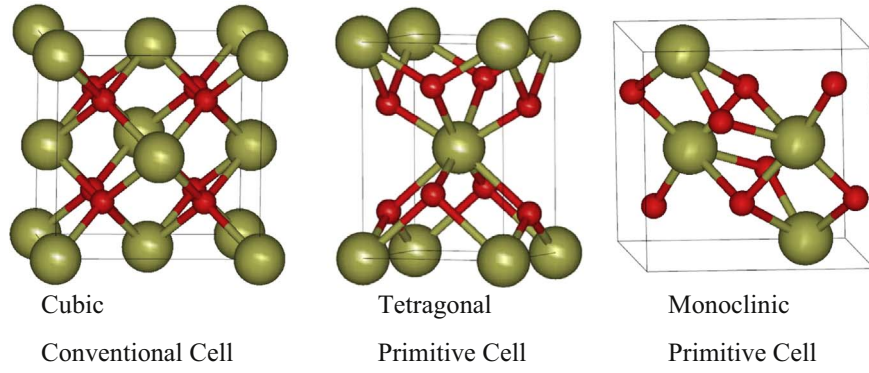
Recently, a related but different class of ferromagnetic materials without magnetic ions, often called *d*<sup>0</sup> ferromagnet, has attracted much attention [3]. This is not only because of its potentially technological application but also because of its scientifically fundamental importance. One of the earliest theoretical studies has predicted ferromagnetism induced by cation vacancies in CaO, where almost localized holes around a Ca vacancy form a high-spin state which couples ferromagnetically to the neighboring spins (vacancy induced ferromagnetism) [4]. Kenmochi et al. [5] later proposed another route of *d*<sup>0</sup> ferromagnetism by showing theoretically that C- and N-doped CaO, i.e., Ca(O,C) and Ca(O,N), becomes half metallic with a room-temperature ferromagnetic transition. In these systems [5], substitutionally doped holes into the valence band, mostly consisting of 2*p* orbitals, form a quasi localized impurity band and they are spin polarized due to the Stoner mechanism [6]. Besides the metal oxides, GaN (or ZnS) with cation defects also shows spin-polarized [7].

Following these studies, extensive theoretical as well as experimental studies have been devoted to confirm and extend these ideas [8,3].

One of the widely studied materials in this regard is HfO<sub>2</sub>. The very first experiment on HfO<sub>2</sub> thin films has suggested a transparent room temperature ferromagnetism [9]. This striking observation has stimulated extensive studies on *d*<sup>0</sup> ferromagnetism in HfO<sub>2</sub>. The experimental results accumulated thus far are rather controversial: some reports even claim no ferromagnetism [10], and others indicate that the appearance of ferromagnetism depends sensitively on experimental conditions [11]. On the theoretical side, the origin of ferromagnetism has not yet been completely understood. Most studies, until now, have focused on effects of cation or/and anion vacancies in HfO<sub>2</sub> [12–15]. Here, we shall show that the surface can also be ferromagnetic.

In this paper, the surface electronic and magnetic properties are systematically studied for cubic, tetragonal, and monoclinic HfO<sub>2</sub> with low index terminations. It is found that (i) stoichiometric surfaces as well as Hf rich non-stoichiometric surfaces are non magnetic, and (ii) O rich non-stoichiometric surfaces are ferromagnetic and metallic except when surface reconstruction by O dimerization takes place. The ferromagnetism found here only for O rich surfaces, i.e., the asymmetric behavior of Hf rich and O rich surfaces, is attributed to the surface electronic states with large O 2*p* spin exchange energy compared to Hf 5*d*. We argue that the present finding offers another pathway to *d*<sup>0</sup> ferromagnetism for non magnetic simple oxides [16]. We also calculate the surface energy and find that the non-stoichiometric surfaces are thermodynamically metastable. This is probably a reason why the observation of ferromagnetism depends on growth conditions [11].

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**Fig. 1.** (Color online) Bulk crystal structures of cubic ( $Fm\bar{3}m$ ), tetragonal ( $P4_2/nmc$ ), and monoclinic ( $P2_1/c$ ) systems. These are three types of polymorphs observed in bulk  $\text{HfO}_2$  with different temperatures [23]. Hf (O) atoms are denoted by large yellow (small red) spheres.

**Table 1**

Lattice constants obtained by the GGA calculations are compared with the experimental values. The angle  $\beta$  between  $a$ - and  $b$ -axes is also included for the monoclinic system.

	Cubic	Tetragonal		Monoclinic			
	a (Å)	a (Å)	c (Å)	a (Å)	b (Å)	c (Å)	$\beta$ (°)
Present	5.066	5.071(3.586)	5.201	5.140	5.197	5.314	99.79
Exp. [25]	5.08	5.155(3.645)	5.285	5.117	5.175	5.292	99.22

## 2. Method and surface atomic structures

The first-principles calculations are performed using the Vienna *ab initio* simulation package (VASP) [17] based on density functional theory with the projector augmented method [18]. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional is adopted [19]. The wave functions are expanded in plane waves with cutoff energy 500 eV. The Brillouin-zone integrations are carried out following the Monkhorst-Pack scheme for the  $k$ -point sampling [20]. The convergence is checked by carefully choosing the cutoff energy and the  $k$ -point sampling. The slab model is adopted to model the surface with periodic boundary conditions, containing a slab of atomic layers and a vacuum region of 10 Å [21,22]. The atomic positions are relaxed for spin unpolarized calculations (forces on each atom are relaxed to less than 0.05 eV/Å), and the obtained structure is used for spin polarized calculations.

Bulk  $\text{HfO}_2$  exhibits three polymorphs, i.e., monoclinic, tetragonal, and cubic, as shown in Fig. 1. It is known that the ground state of bulk  $\text{HfO}_2$  is monoclinic [23], whereas the ground state of thin films  $\text{HfO}_2$  is most likely monoclinic or tetragonal, depending on growth conditions [24]. To check our calculations, we have first calculated the lattice constants for each bulk system, and the results are summarized in Table 1. Our GGA calculations for the lattice constants reproduce the experimental values [25] within less than a few %.

Here, we consider thirty different  $\text{HfO}_2$  surfaces, cubic and tetragonal surfaces with all possible low index terminations and monoclinic surfaces with representative low index cuts, and they are all shown in Fig. 2 (without atomic position relaxation) and in Fig. 3 (with atomic position relaxation). Table 2 summarizes the number of atoms and stoichiometry for all surfaces considered. Here, “c”, “t”, and “m” stand for cubic, tetragonal, and monoclinic, respectively. It is observed in Fig. 3 that the dimerization of O atoms occurs at the surfaces of t:11

$\bar{2}$ -OO, m: $\bar{1}$  11-Hf, m: $\bar{1}$  11-2O, m: $\bar{1}$  11-10O, m: $\bar{1}$  11-11O, and m: $\bar{1}$  11-12O. Although the surfaces studied here are limited, we expect that our conclusion is general and remains valid for other surfaces of  $\text{HfO}_2$  for reasons discussed below.

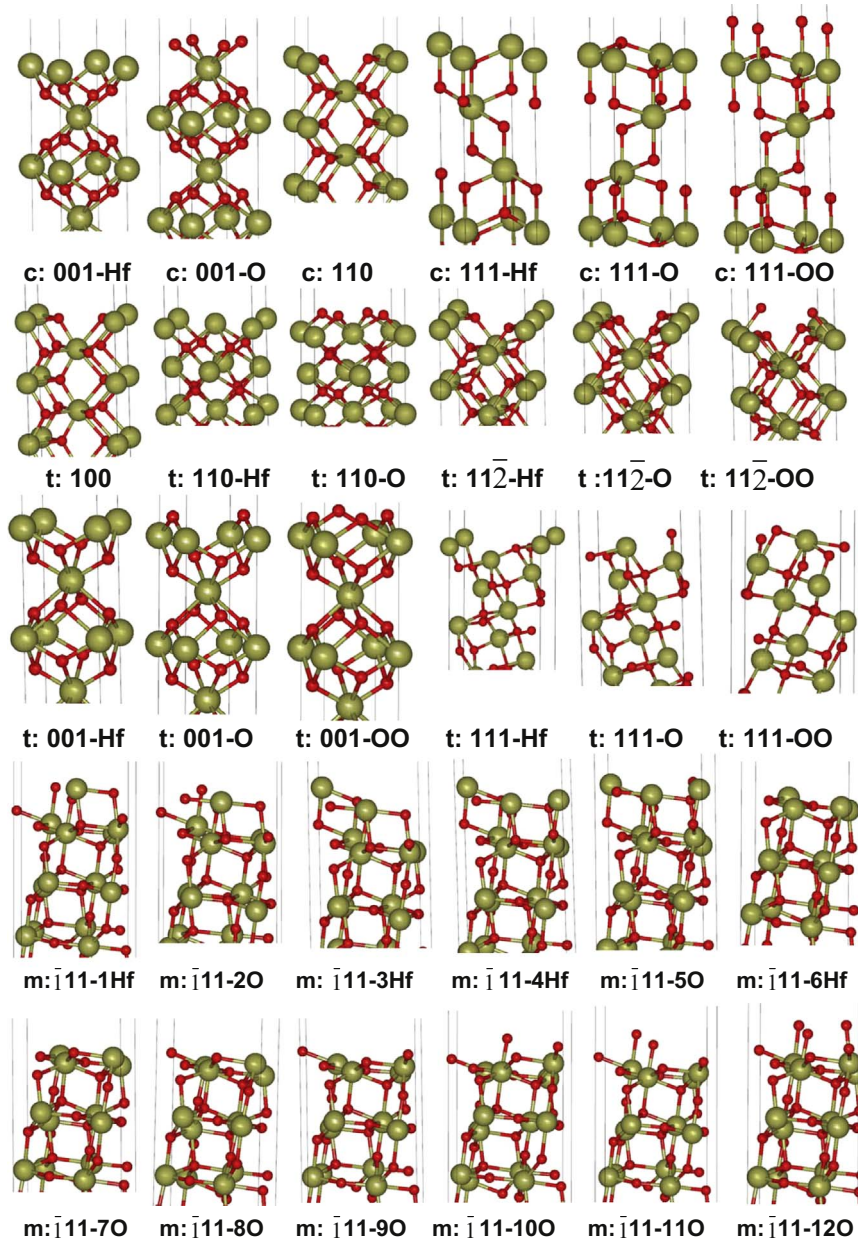
## 3. Results and discussion

Our main results are summarized in Tables 2, 3. Table 3 lists all systems for which the ground state is ferromagnetic with induced magnetic moment ( $M$ ). The main finding is that i) the ground state is non magnetic for stoichiometric and Hf rich non-stoichiometric surfaces, and ii) the ground state is ferromagnetic for O rich non-stoichiometric surfaces [26]. We also find that for O rich surfaces sometimes surface reconstruction induces O dimerization [24], which favors a non magnetic state. However, even for these cases, a ferromagnetic ground state is still found when the atomic position relaxation is limited.

Fig. 4(a) shows total densities of states (DOS) for spin up and spin down electrons calculated for a cubic O rich surface named c:111-OO [Fig. Fig. 6(c)]. It is clearly found in Fig. 4(a) that the ground state is ferromagnetic and metallic. Because of the charge neutrality condition,  $N_h = 2N_O - 4N_{\text{Hf}}$  holes per unit cell are introduced for O rich non-stoichiometric surfaces ( $N_h=4$  for c:111-OO), where  $N_O$  ( $N_{\text{Hf}}$ ) is the number of O (Hf) atoms per unit cell. Partial DOS for O and Hf atoms shown in Figs. 4(b) and 4(c) indicates that these holes are introduced in the valence band formed mainly by O  $2p$  orbitals, and they are spin polarized with  $M \approx 3.7\mu_B$ , slightly less than the full spin polarization ( $N_h\mu_B$ ) of the holes. We find that all the ferromagnetic ground states listed in Table 3 are metallic, and for some cases they are even half metallic.

To determine which oxygen is responsible for the ferromagnetism, we next calculate layer by layer partial DOS for O atoms in Fig. 5. We can clearly find in Fig. 5 that the spin polarization occurs mostly at the two outermost O layers. Indeed,  $M$  in the 4th O layer is zero and the DOS for the 4th O layer very much resembles that for the bulk system [21]. It is also interesting to notice that the partial DOS for O  $2s$  at the 1st layer (located at around 16–17 eV) is split for spin up and spin down electrons by about 2 eV. This splitting is simply because of a finite  $M$  induced mainly by O  $2p$  spin polarization at the surface, and it gradually disappears in the deeper layers. From these results, we conclude that the ferromagnetic metal found here is caused by spin polarization of mostly O  $2p$  holes at the outermost O layers.

Let us now examine the origin of this surface ferromagnetic metal. For this purpose, it is important to notice that there exist rather sharp peaks (i.e., large DOS) around the Fermi energy in the



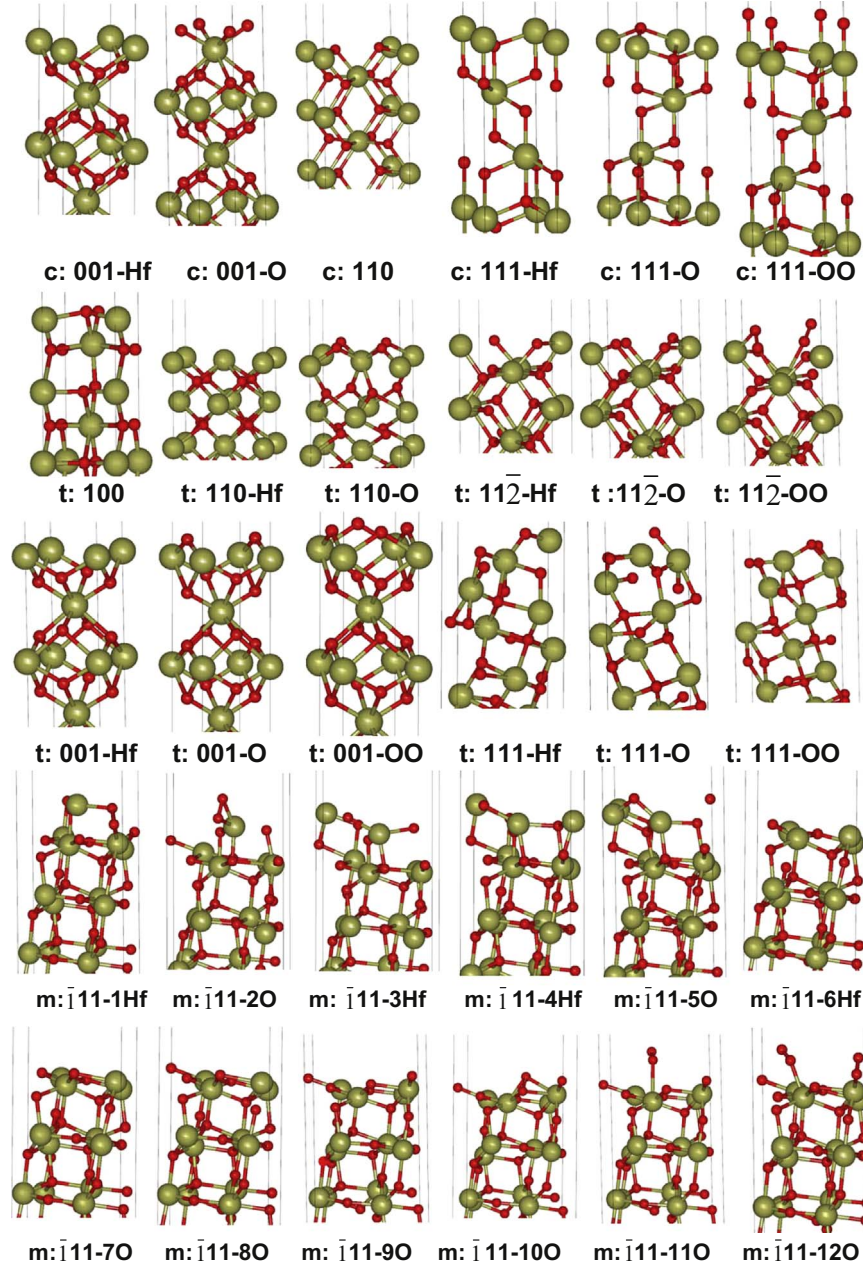
**Fig. 2.** (Color online) Halves of symmetrical slabs without relaxing atomic positions. Hf (O) atoms are indicated by large yellow (small red) spheres. “c”, “t”, and “m” stand for cubic, tetragonal, and monoclinic, respectively.

partial DOS for O  $2p$  holes of the 1st and 2nd O layers, as shown in Fig. 5. This immediately implies that the ferromagnetism is due to a Stoner type mechanism. To better understand the origin, the spin unpolarized calculations are performed, and the obtained partial DOS for different O atoms is shown in Figs. 6(a). As expected, O  $2p$  orbitals mostly in the 1st and 2nd layers are the ones crossing the Fermi energy, and the DOS for these layers show large peaks at the Fermi energy. This feature is also consistent with the momentum resolved band dispersion shown in Fig. 6(b). Indeed, we find in Fig. 6(b) that the band crossing the Fermi energy has a relatively small width of dispersion.

Although it is reasonable, the above argument alone does not explain the asymmetric behavior of O rich surfaces and Hf rich surfaces [27]. Notice here that electrons are introduced for Hf rich

non-stoichiometric surfaces due to the charge neutrality condition [21]. To understand this asymmetry, here a Gedanken system is considered where holes (electrons) are injected in bulk  $\text{HfO}_2$  by removing (adding) electrons and at the same time a jellium background is considered to compensate the injected charges [28]. Fig. 7 shows the results for  $M$  calculated for bulk  $\text{HfO}_2$  in monoclinic structure [29]. The electron-injection, which introduces electrons into the conduction band formed mostly by Hf  $5d$  orbitals, does not induce a finite  $M$ . In sharp contrast, even a small amount of holes ( $\geq 0.2$  per O) is enough to spin polarize with the full magnetic moment. This asymmetric behavior is understood by large difference of the spin exchange splitting energy (energy gain)  $J$  for O  $2p$  orbitals ( $\sim 3.03$  eV) and Hf  $5d$  orbitals ( $\sim 1.04$  eV) with  $M = 2\mu_B$  [28]. The larger  $J$  for O  $2p$  orbitals along with the wider spreading  $5d$  atomic





**Fig. 3.** (Color online) Halves of Symmetrical slabs with relaxed atomic positions. Hf (O) atoms are indicated by large yellow (small red) spheres. “c”, “t”, and “m” stand for cubic, tetragonal, and monoclinic, respectively.

orbital compared to the  $2p$  atomic orbital [28] is the reason why the hole-injection can spin polarize much easier, in spite of the fact that the calculated band width of the conduction band seems even slightly smaller than that of the valence band [21]. Besides, for the O excess surfaces, spin polarizability is expected to be more enhanced because of the large DOS around the Fermi energy for the outermost surface layers [Figs. 5 and Figs. 6(a)], certainly favoring the Stoner's criterion for ferromagnetism [6].

Finally, let us examine the surface energy for all the thirty different surfaces studied here. Details of the calculations are described in Ref. [21], and here only the main results are shown in Fig. 8 for cubic, tetragonal, and monoclinic structures. We find that the stoichiometric surfaces are stablest thermodynamically for all cases. A similar conclusion has been reported previously based on

spin unpolarized calculations [21,24]. Although it is thermodynamically metastable, non-stoichiometric surfaces would be realized under restricted circumstances using, e.g., pulsed laser deposition or molecular beam epitaxy [30].

Experimentally, the emergence of ferromagnetism in  $\text{HfO}_2$  is still under debate. The evidence for the ferromagnetism have been reported much often in thin films and nano sized crystals [11], but it is less certain in a bulk form [10]. Intrinsic cation or anion vacancies have been considered as a possible mechanism of the ferromagnetism [9,12]. Recently, it has been reported that non-stoichiometric conditions are essential to realize such ferromagnetically coupled magnetic vacancies [13]. Here, we propose O excess surfaces as another possible mechanism for the ferromagnetism. It should be emphasized that the surface ferromagnetism found here is

**Table 2**

Thirty different surfaces studied. Hf:O in the second column is the number of Hf and O atoms in the slab.

Cubic	Hf:O	stoichiometry	magnetism
c:001-Hf	7:12	Hf rich	non magnetic
c:001-O	7:16	O rich	magnetic
c:110	9:18	stoichiometric	non magnetic
c:111-Hf	7:12	Hf rich	non magnetic
c:111-O	7:14	stoichiometric	non magnetic
c:111-OO	7:16	O rich	magnetic
Tetragonal	Hf:O	stoichiometry	magnetism
t:100	9:18	stoichiometric	non magnetic
t:110-Hf	10:16	Hf rich	non magnetic
t:110-O	10:24	O rich	magnetic
t:001-Hf	7:12	Hf rich	non magnetic
t:001-O	7:14	stoichiometric	non magnetic
t:001-OO	7:16	O rich	magnetic
t:11 $\bar{2}$ -Hf	14:24	Hf rich	non magnetic
t:11 $\bar{2}$ -O	14:28	stoichiometric	non magnetic
t:11 $\bar{2}$ -OO	14:32	O rich	(non) <sup>a</sup> magnetic
t:111-Hf	16:30	Hf rich	non magnetic
t:111-O	15:30	stoichiometric	non magnetic
t:111-OO	15:32	O rich	magnetic
Monoclinic	Hf:O	stoichiometry	magnetism
m: $\bar{1}$ 11-1Hf	22:46	O rich	(non) <sup>a</sup> magnetic
m: $\bar{1}$ 11-2O	18:40	O rich	magnetic
m: $\bar{1}$ 11-3Hf	20:40	stoichiometric	non magnetic
m: $\bar{1}$ 11-4Hf	22:40	Hf rich	non magnetic
m: $\bar{1}$ 11-5O	22:42	Hf rich	non magnetic
m: $\bar{1}$ 11-6Hf	20:34	Hf rich	non magnetic
m: $\bar{1}$ 11-7O	20:36	Hf rich	non magnetic
m: $\bar{1}$ 11-8O	20:38	Hf rich	non magnetic
m: $\bar{1}$ 11-9O	20:40	stoichiometric	non magnetic
m: $\bar{1}$ 11-10O	20:42	O rich	(non) <sup>a</sup> magnetic
m: $\bar{1}$ 11-11O	20:44	O rich	magnetic
m: $\bar{1}$ 11-12O	20:46	O rich	(non) <sup>a</sup> magnetic

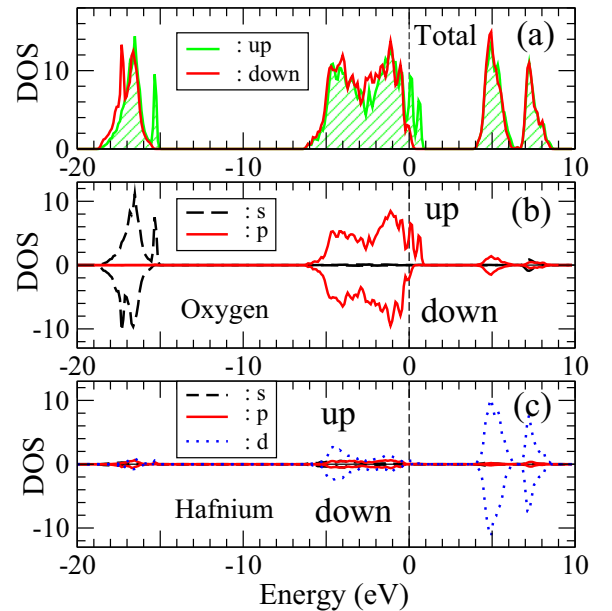
<sup>a</sup> When the atomic positions are relaxed (not relaxed), the ground state is non magnetic (magnetic).

**Table 3**

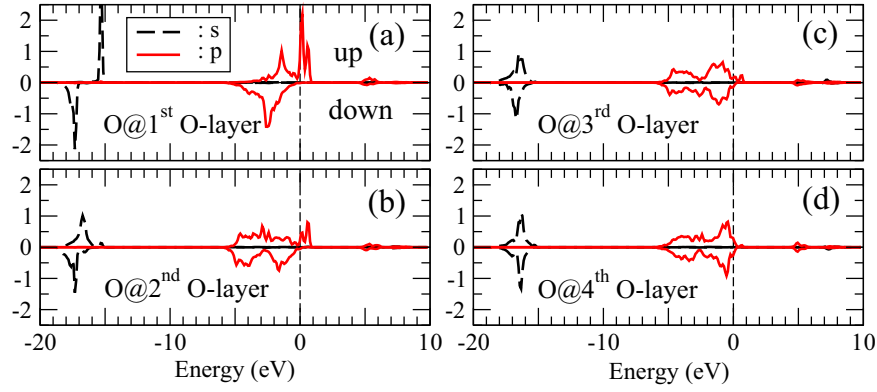
Induced magnetic moments ( $M$ ) for O rich non-stoichiometric surfaces. Other surfaces (stoichiometric surfaces and Hf rich non-stoichiometric surfaces) studied are all non magnetic. Hf:O is the number of Hf and O atoms in the slab.  $\Delta E$  is the ground state energy difference between spin polarized and non spin polarized calculations.

Cubic ( $Fm\bar{3}m$ )	Hf:O	$M$ ( $\mu_B$ )	$\Delta E$ (eV)
c:001-O	7:16	3.6	-0.19
c:111-OO	7:16	3.7	-1.06
Tetragonal ( $P4_2/nmc$ )	Hf:O	$M$ ( $\mu_B$ )	$\Delta E$ (eV)
t:110-O	10:24	8.0	-0.58
t:001-OO	7:16	4.0	-0.38
t:11 $\bar{2}$ -OO <sup>a</sup>	14:32	0.0 (8.0)	-(-2.62)
t:111-OO	15:32	4.0	-0.18
Monoclinic ( $P2_1/c$ )	Hf:O	$M$ ( $\mu_B$ )	$\Delta E$ (eV)
m: $\bar{1}$ 11-1Hf <sup>a</sup>	22:46	0.0 (4.0)	-(-0.80)
m: $\bar{1}$ 11-2O <sup>a</sup>	18:40	4.0 (8.0)	-1.06 (-1.69)
m: $\bar{1}$ 11-10O <sup>a</sup>	20:42	0.0 (4.0)	-(-1.34)
m: $\bar{1}$ 11-11O <sup>a</sup>	20:44	4.0 (8.0)	-1.86 (-3.14)
m: $\bar{1}$ 11-12O <sup>a</sup>	20:46	0.0 (12.0)	-(-5.25)

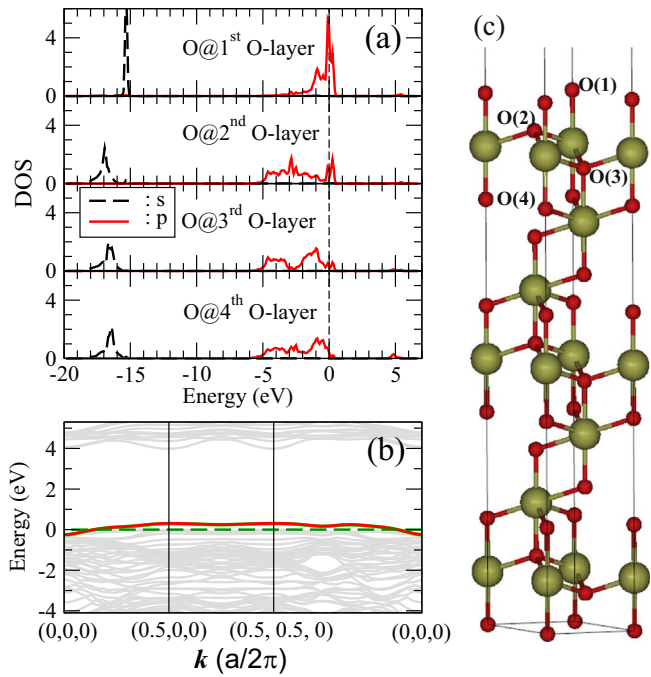
<sup>a</sup> Surface reconstruction with O dimerization is observed [24]. When this occurs, the ground state very often becomes non magnetic. However, when the atomic position relaxation is not allowed, the ground state turns to be ferromagnetic with  $M$  and  $\Delta E$  denoted in parentheses.



**Fig. 4.** (Color online) DOS (states/eV cell) for c:111-OO surface [see Fig. 3 and also Fig. 6(c)]. (a) Total DOS for spin up and down electrons denoted by green and red lines, respectively. (b) O 2s and 2p partial DOS (denoted by black dashed and red solid lines, respectively) for spin up and down electrons. (c) Hf 5d, 6s, and 6p partial DOS (denoted by blue dotted, black dashed, and red solid lines, respectively) for spin up and down electrons. Fermi energy is indicated by vertical dashed lines at zero energy.

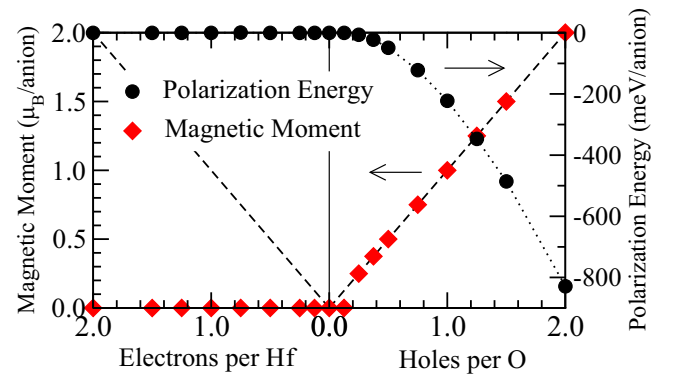


**Fig. 5.** Layer-by-layer O  $2s$  and  $2p$  partial DOS (states/eV atom) for c:111-OO. Fermi energy is indicated by vertical dashed lines at zero energy. Positions of O layers are indicated in Fig. 6 (c).



**Fig. 6.** (Color online) (a) Layer-by-layer O  $2s$  and  $2p$  partial DOS (states/eV atom) for c:111-OO calculated with no spin polarization. Fermi energy is indicated by a vertical dashed line at zero energy. (b) Momentum resolved band dispersions for spin unpolarized c:111-OO. Fermi energy is denoted by a horizontal green dashed line at zero energy. The energy band crossing Fermi energy is indicated by a red solid line.  $a$  is the lattice constant. (c) The slab of c:111-OO without relaxing atomic positions. O (Hf) atoms are denoted by small red (large yellow) spheres. The locations of O layers are also indicated.

distinct from the vacancy-induced ferromagnetism, even though both are most likely relevant for  $\text{HfO}_2$ , because the former is induced by large O  $2p$  spin exchange energy. Although these ferromagnetic surfaces are thermodynamically metastable, they might exist in epitaxially thin film samples [24]. This is probably a reason why it is difficult to find ferromagnetism in perfect crystals [10]. This is also consistent with the experimental observations in that the observed magnetic moments are independent of the thickness of films [11].

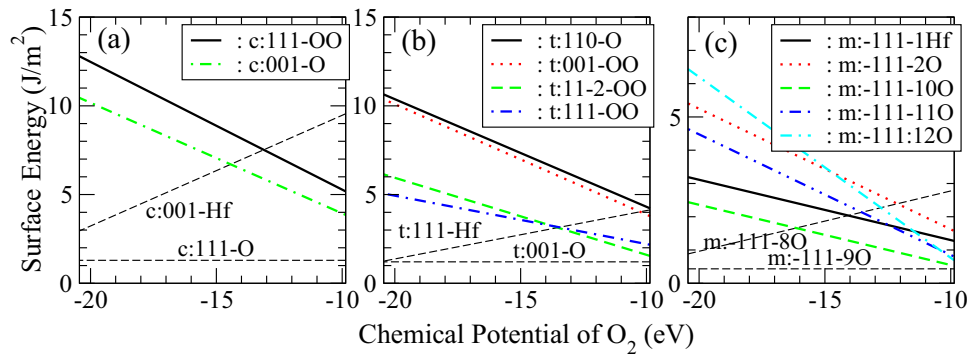


**Fig. 7.** Magnetic moment ( $M$ ) and polarization energy ( $\Delta E$ ) of electron- and hole-injected bulk  $\text{HfO}_2$  in monoclinic structure.  $\Delta E$  is the ground state energy difference between spin polarized and unpolarized calculations when  $M$  is finite ( $\Delta E = 0$  when  $M = 0$ ). Dashed lines indicate the expected magnetic moments when the injected electrons or holes are fully spin polarized.

Here, we have only considered perfect and simple surfaces, and more complex surfaces with a wide range of surface reconstructions remain to be studied in future.

#### 4. Conclusion

We have studied surface electronic and magnetic properties of  $\text{HfO}_2$ . It was found that O rich non-stoichiometric surfaces are ferromagnetic and metallic, while Hf rich non-stoichiometric surfaces and stoichiometric surfaces are non magnetic. The asymmetric behavior of O rich and Hf rich surfaces is attributed to O surface electronic states with large O  $2p$  spin exchange energy. The surface ferromagnetism found here offers an alternative mechanism for the still controversial ferromagnetism observed in  $\text{HfO}_2$ . This mechanism can provide another pathway to novel  $d^0$  ferromagnetism for non magnetic oxides in general, and should be applied to other seemingly simple oxides in which unexpected ferromagnetism has been observed [31].



**Fig. 8.** Surface energies of the relaxed surfaces in (a) cubic, (b) tetragonal, and (c) monoclinic structures. For clarity, only the lowest surface energies are plotted for stoichiometric and Hf rich non-stoichiometric surfaces.

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