Abstract. Using first-principles simulations based on density functional theory, we demonstrate that surfaces of simple oxides can be ferromagnetic without involving magnetic transition metal ions, thus called $d^0$ ferromagnetic surface. We take cubic HfO$_2$ as an example to show that the surface electronic states depend critically on the surface termination and only O rich non-stoichiometric surfaces are ferromagnetic. Systematic studies of various surfaces with different surface indexes and terminations indicate that the O surface electronic states are spin polarized due to the large O 2$p$ spin exchange energy. We argue that the mechanism proposed here is rather general and can be applied to other simple oxides such as SrO.

1. Introduction

It is well known that materials which show bulk magnetism contain almost always magnetic ions i.e., transition metals, rare earth elements, or some of actinide elements [1]. For example, various transition metal oxides exhibit a wide range of magnetic properties, which are caused by unpaired $d$ electrons inducing a finite local magnetic moment [2]. In contrast to this class of magnetic materials, a great deal of effort has been devoted to attempting to make bulk magnetic materials without involving magnetic ions (often called $d^0$ magnetism) [3]. For example, one of the recent theoretical studies has demonstrated that a small amount of cation vacancies can induce ferromagnetism in CaO (vacancy induced ferromagnetism) [4]. Kenmochi et al. [5] have then shown theoretically that C- and N-doped CaO becomes ferromagnetic and half metallic, where substitutionally doped holes in O 2$p$ valence band form quasi localized impurity band which are spin polarized due to Stoner mechanism [6]. Following these reports, there have been extensive studies both theoretically and experimentally to confirm and extend these ideas [3].

In this paper, using first-principles simulations based on density functional theory (DFT), we shall demonstrate that surfaces of simple oxides can be ferromagnetic, which we think offers another route to $d^0$ ferromagnetism. We take HfO$_2$ as such examples and show that only the O rich non-stoichiometric surfaces are indeed ferromagnetic. We find that the magnetism appears at a few outmost O layers where holes are introduced into the O 2$p$ originated valence band. We attribute this magnetism to the large O 2$p$ spin exchange energy, which should be as large as
that for 3d transition metals [3]. We believe that the mechanism proposed here, \(d^0\) ferromagnetic surface, is general and can be applied to other simple oxides such as SrO.

2. Numerical Method
The calculations are carried out using the projector augmented method [7] and the generalized gradient approximation (GGA-PBE) implemented in the Vienna \textit{ab initio} simulation package [8]. The wave functions are expanded in plane waves up to a cutoff energy of 500 eV, and Brillouin-zone integrations are approximated by using the special \(k\)-point sampling of Monkhorst-Pack scheme [9]. Convergence is checked by carefully choosing the cutoff energy and the \(k\)-point sampling. The surface is modeled by a slab with periodic boundary conditions to the surface supercell which includes a slab of atomic layers and a vacuum region of 10 Å [10, 11]. The atomic positions are relaxed for spin non-polarized and polarized calculations until the force acting on each atom becomes less than 0.01 eV/Å. It is known that bulk HfO\(_2\) has three polymorphs (monoclinic, tetragonal, and cubic) and the ground state is monoclinic [12], whereas the ground state of thin films is most likely monoclinic or tetragonal depending on growth conditions [13]. We have considered thirty different HfO\(_2\) surfaces, cubic and tetragonal surfaces with all possible low index terminations, and representable cuts for monoclinic surfaces. In this paper, we shall focus one prototype surface of cubic HfO\(_2\) with [111] cut and O termination (named C:111-OO), as shown in Fig. 1 (a). The other results will be presented elsewhere.

3. Results
Let us first examine the atomic structure of the surface. We relax the atomic positions using spin polarized calculations, and the results are shown in Fig. 1 (b). For comparison, the ideal structure before the relaxation is also shown in Fig. 1 (a). Fig. 1 indicates that there is only slight movement of the outmost atoms at the surfaces.

![Figure 1](Color online) The symmetrical slabs of C:111-OO (a) before and (b) after atomic position relaxation. Here, O and Hf are denoted by small and large spheres, respectively. The number of O (Hf) atoms in the supercell is 7 (16).

Next, we shall study the electronic structure. Fig. 2 summarizes the results of the density of states (DOS) for spin up and spin down electrons. It is clearly seen in Fig. 2 (b) that the ground state is ferromagnetic. We can also notice in Fig. 2 (a) that the Fermi level is shifted downward to the top of the valence band when it is compared to the bulk electronic structure [11]. To better understand the electronic structure, it is important to note that, because of the charge neutrality condition, \(N_h = 2N_O - 4N_{Hf}\) holes per supercell for the O rich non-stoichiometric surfaces are introduced, \(e.g., N_h = 4\) for the present case. Here, \(N_O (N_{Hf})\) is the number of O (Hf) atoms per supercell. The partial DOS’s for O and Hf atoms are plotted in Figs. 2 (c) and
respectively, which clearly show that these holes are introduced mostly into the O 2p based valence band. We find that the induced magnetic moment is $M = 4\mu_B$, i.e., the doped holes being fully spin polarized for the present surface.

![Figure 2.](image)

Figure 2. (Color online) Density of states (DOS) (states/eV cell) for C:111-OO surface. (a) Total DOS (black lines). (b) DOS for spin up and spin down electrons denoted by green (hatched) and red (unhatched) lines, respectively. (c) O 2s and 2p partial DOS for spin up and spin down electrons. (d) Hf 5d, 6s, and 6p partial DOS for spin up and spin down electrons. For comparison, total DOS for the bulk cubic HfO$_2$ is also plotted by green shadow in (a) [11]. Fermi level is denoted by vertical dashed lines.

Let us now examine which oxygen is responsible for the magnetism. For this purpose, we show in Fig. 3 the partial DOS’s calculated layer by layer for different O atoms, the locations of which are indicated in Fig. 1 (b). These results clearly reveal that the finite spin polarization occurs at the outmost O atoms, and the spin polarization diminishes almost completely in the 4th O layers. It is also interesting to notice that the O 2s levels of spin up and spin down electrons are split, for example, as clearly seen in Fig. 3 (a), and gradually disappears for inner O layers. The split of O 2s levels is simply because of the presence of a finite magnetic moment induced in O 2p which then affects O 2s as an effective magnetic filed.

Finally, let us consider the origin of this ferromagnetism. To understand its origin, we consider a Gedanken system where holes are injected into the bulk HfO$_2$ by removing electrons and using a jellium background to keep the total charge neutral [14]. For this ”artificial” system, we find that even a small amount of holes is enough to spin polarize the ground state. The finite spin polarization is caused by the large spin exchange energy for O 2p, which favors ferromagnetic spin alignment [14]. We attribute the same mechanism to the origin of the surface ferromagnetism found in this paper. In fact, we do find that the ground states of other [111] surfaces for cubic HfO$_2$ with different terminations (stoichiometric and Hf rich non-stoichiometric surfaces) are non magnetic, namely, only the O rich non-stoichiometric surfaces are ferromagnetic. We have carried out detailed studies and the results will be reported in a separate paper.

4. Summary
Using first-principles simulations based on DFT, we have demonstrated that surface electronic states of simple oxides can be spin polarized to be surface ferromagnetic. Taking cubic HfO$_2$ as a typical example, we have shown that the O rich non-stoichiometric surfaces are indeed ferromagnetic. This is in sharp contrast to stoichiometric and Hf rich non-stoichiometric
surfaces where the ground states are both non magnetic. We have attributed the origin of the ferromagnetism to the large spin exchange energy of O $2p$. We believe that the mechanism proposed here for $d^0$ ferromagnetic surface is general and can be applied to other simple oxides such as SrO. The systematic study is now in progress and will be reported elsewhere. Lastly, it should be interesting to note that a recent DFT calculation has reported a possible ferromagnetic ground state of ZnO honeycomb nano sheets for which the magnetism appears only at the edge where oxygen atoms terminate the zigzag nano ribbon [15]. We think that the ferromagnetism in zigzag ZnO nano ribbons shares some similarities with surface $d^0$ ferromagnetism for simple oxides studied in this paper, and might be explained also by the large spin exchange energy of O $2p$.

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Figure 3. (Color online) Layer-by-layer O 2s and 2p partial DOS (states/eV cell) for C:111-OO. Fermi level is denoted by vertical dashed lines. Loci of layers are denoted in Fig. 1 (b).