

Charging-induced stabilization of ferroelectric orthorhombic HfO₂ films: first-principles study on key growth conditions

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Abstract

Orthorhombic Pca2₁ HfO₂ (ortho1-HfO₂) films are attractive systems for ferroelectric nonvolatile memory and tunnel-junction devices. However, since the ortho1-HfO₂ is not a thermodynamically stable phase, it is still unclear what mechanisms stabilize this phase. In this work, we showed by the first-principles calculation that the positive charging of HfO₂ layers occurs due to oxygen vacancies (Vo's) and stabilizes the ortho1-HfO₂ owing to the Madelung-energy gain, and such charging is markedly accelerated by the cation-atom doping.

1. Introduction

Ferroelectric orthorhombic Pca2₁ HfO₂ (ortho1-HfO₂) films are attractive systems for realizing future nonvolatile memory and tunnel-junction devices [1]. However, since the ortho1-HfO₂ is not a thermodynamically stable phase, the cooling from a high-temperature tetrahedral phase normally results in a non-ferroelectric monoclinic HfO₂ (mono-HfO₂) and we need some special treatments to grow ferroelectric ortho1-HfO₂ films; they are, for example, (i) the “metal cap” structure with electrodes like TiN [2] and (ii) the doping of cation atoms such as Si [3]. On the other hand, previous theoretical calculations concluded that the most stable phase is mono-HfO₂ or ortho2-HfO₂ (Pnm2₁) in case of bulk or thin film [4,5]. Therefore, it is still unclear what mechanism stabilizes the ortho1-HfO₂ phase.

In this work, we propose a new mechanism to realize the ortho1-HfO₂; “the charging of HfO₂ layers”. It is well known that HfO₂ contains many oxygen vacancies (Vo's), around a few percents in normal growth condition, and such Vo's are easily ionized when HfO₂ layers are attached to p-metal electrodes like TiN [6]. In this view, we naturally wonder whether the charging of HfO₂ layers promotes the ortho1-HfO₂ generation. Therefore, we study the charging properties of HfO₂ by the first-principles calculation and demonstrate that, when the hole carriers are injected into HfO₂, the ortho1-HfO₂ phase becomes the most stable as shown in Fig.1.

2. Calculation Model and Method

In this work, we compare the stability of ortho1-, ortho2-, and mono-HfO₂ phases, using large (HfO₂)₃₂ bulk and thin-film unit cells shown in Fig.2. 1.6-6.2% Vo's and 3.2% cation dopants (X=Si,Ge,Ga,Y at Hf sites) are inserted in these cells. The stability of various phases against the positive charging is evaluated by removing electrons from these cells and calculating the ‘charged’ formation energy.

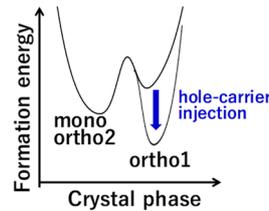


Fig.1 The present scenario to realize ferroelectric ortho1-HfO₂; the positive charging makes ortho1-HfO₂ films the most stable.

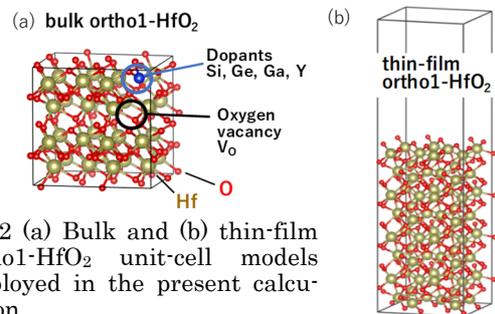


Fig.2 (a) Bulk and (b) thin-film ortho1-HfO₂ unit-cell models employed in the present calculation.

Atomic and electronic structures are calculated by the standard first-principles method in the density functional theory, using the VASP code [7]. In each case of charging, all atom positions and unit-cell sizes are optimized. We use the GGA-PBE exch-corr. functional, the Γ -k-point sampling of electron density, and the 500eV cut-off for wave-function expansion. Other calculation details are described in our previous works [8,9].

3. Results and Discussions

Charging-induced stabilization of ortho1-HfO₂ films

First, we consider how the positive charging changes the stability of various phases. Fig.3(a) shows the formation energy of ortho1-HfO₂ bulk with 6.2% Vo's relative to that of mono-HfO₂, as a function of the charging value of Vo. For reference, such energies are also shown for HfO₂ without Vo and ortho2-HfO₂. Note that a Vo prefers to be ionized positively by “+2” [6]. In case of neutral, the ortho1-HfO₂ is unstable, consistent with previous theories and experiments [1,4]. However, it is clearly seen that the +2 Vo charging stabilizes the ortho1-HfO₂ bulk layers, as schematically shown in Fig.1. As shown in Fig.3(b), the similar stabilization of the ortho1-HfO₂ is seen in case of thin films.

Such stabilization is understood by considering the Madelung energy, $E_M = -\alpha \sum_G \rho_{Hf}(G) \rho_O(G) / G^2$, because HfO₂ is an ionic material. Here, we use the momentum-space formula, α is the Madelung constant, G is the reciprocal lattice, and $\rho_O(G)$ is the Fourier transform of O-

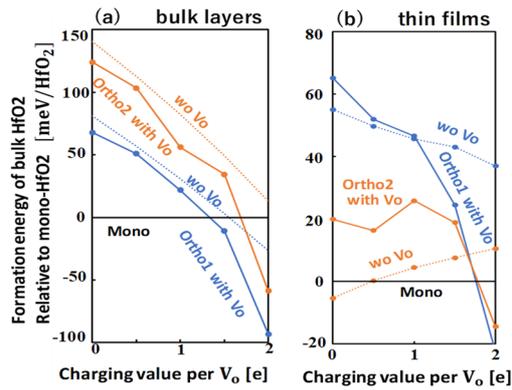
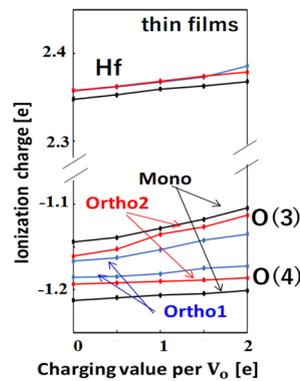


Fig.3 Formation energies ortho1-HfO₂ relative to mono-HfO₂ as a function of Vo charging values, for the cases of (a) bulk layers and (b) thin films. Solid lines correspond to the case with Vo's.

Fig.4 Ionization charges of Hf, O(3), and O(4) atoms in various HfO₂ thin films, as a function of Vo charging value. For bulk layers, we obtain similar results.

The uniform O-charge distribution, i.e., the small difference between O(3) and O(4), stabilizes the ortho1-HfO₂ phase compared to other phases.



atom ionization charge. Fig.4 shows the ionization charges of Hf, three-coordinated O(3), and four-coordinated O(4) atoms, as a function of the Vo charging value. It should be noted that O(3) and O(4) atoms have different charges reflecting the different Hf-O distances in different crystal structures. We note that the O charge is inhomogeneous for the mono-HfO₂, while uniform for the ortho1-HfO₂. Since the Madelung energy gain E_M becomes large for the uniform charge distribution having large $\rho_O(G)$ for small G , the ortho1-HfO₂ has the largest energy gain and is stabilized with increasing the charging.

Effects of cation-atom doping

Next, we consider the effects of cation-atom doping on the stability. Fig.5(a) shows the formation energy of Vo in HfO₂ with and without dopants, where we found that the Vo prefers to locate nearest to the dopant X, thus producing a Vo+X complex. The dopants largely decrease the formation energy and thus increase the Vo density. This is because the Hf-O bond is much stronger than the X(dopant)-O bond and thus the generation of Vo by breaking the X-O bond easily occurs nearest to the dopants.

Then, we consider how the charging of Vo+X complex affect the stability. Fig.5(b) shows the formation energy of the ortho1-HfO₂ with 3.2% Vo+X complex, in neutral and +2-charged cases. It is seen that the Vo+Si and Vo+Ge complexes remarkably decrease the energy, compared to the case of simple Vo. One major reason for this stabilization is

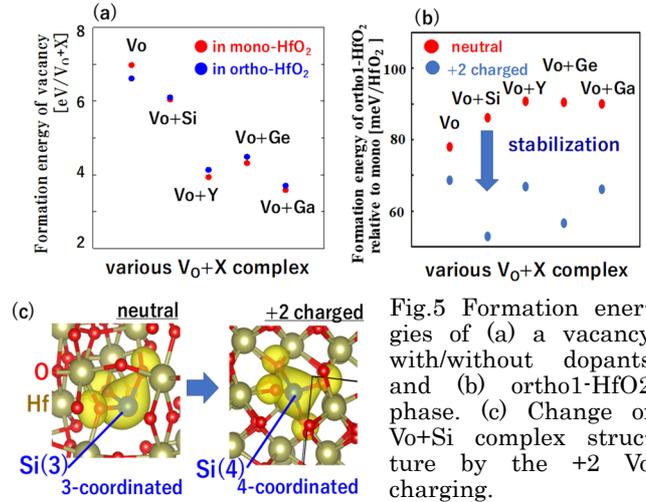


Fig.5 Formation energies of (a) a vacancy with/without dopants and (b) ortho1-HfO₂ phase. (c) Change of Vo+Si complex structure by the +2 Vo charging.

the changes of atomic and electronic structures inside the Vo+X complex. As shown in Fig.5(c), Si is bonded with three O atoms when neutral, while Si produces four strong Si-O bonds when +2 charged. As a result, the ortho1-HfO₂ with Vo+X complexes is more stabilized by the positive charging.

Key processes to realize ortho1-HfO2

Finally, we explain how the present charging scenario is related to key processes for the ortho1-HfO₂ growth found in experiments [2,3]. When HfO₂ films are attached to p-metal electrodes, the electron transfer from Vo to electrodes gains the energy and accelerates both the generation and ionization of Vo. In addition, such energy gain becomes large when the films are enough thin. We also showed that the cation-atom doping increases the Vo density to produce Vo+X complexes, which efficiently ionize HfO₂ layers and stabilize the ortho1-HfO₂. In this way, the present results clearly explain the experiments, indicating that the charging of HfO₂ can be a leading factor to realize the ortho1-HfO₂.

4. Conclusions

In this work, by the first-principles calculation, we clarified that the positive charging of oxygen vacancies in HfO₂ films stabilizes the ferroelectric ortho1-HfO₂ phase owing to the Madelung-energy gain by its uniform charge distribution. Moreover, we showed that the cation-atom doping increases the vacancy density and accelerates the charging.

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