First-principles study on the concentrations of native point defects in high-dielectric-constant binary oxide materials

J. X. Zheng¹, G. Ceder², and W. K. Chim¹,³

¹ Singapore-MIT Alliance, 4 Engineering Drive 3, Singapore 117576
² Department of Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139-66307, USA
³ Department of Electrical and Computer Engineering, National University of Singapore, 4 Engineering Drive 3, Singapore 117576

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* Corresponding author: e-mail elecwk@nus.edu.sg

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1 Introduction

As feature sizes of the metal–oxide–semiconductor field-effect transistor device continue to shrink towards nanometer dimensions, high-dielectric-constant (high-k) materials are urgently needed to replace the silicon dioxide (SiO₂) gate dielectric. According to the International Technology Roadmap for Semiconductors, a progression from hafnium-based dielectrics to Group III and rare-earth oxides to ternary oxides might be required [1]. It is known that there are higher concentrations of pre-existing defects in high-k gate dielectrics that cause threshold voltage instability and give rise to the charge scattering of channel carriers, which in turn reduces the channel carrier mobility [2]. The origin of these imperfections has been attributed to oxygen defects [3–8]. In the present article, we extend our previous work [9, 10] to investigate the dominant point defects under the constraint of charge neutrality in bulk hafnium oxide (HfO₂), zirconium oxide (ZrO₂), yttrium oxide (Y₂O₃) and lanthanum oxide (La₂O₃). By calculating the defect concentrations, our results support the speculation that oxygen-related defects are the dominant point defects in these binary high-k oxides. In HfO₂ and ZrO₂, oxygen Frenkel pairs are particularly likely to form. There are higher concentrations of charged oxygen defects in Y₂O₃ and La₂O₃ than in HfO₂ and ZrO₂.

2 Computational methods

The calculations are based on the density functional theory (DFT) in the generalized gradient approximation using the projector augmented wave method [11, 12], as implemented in the VASP (Vienna ab-initio simulation package) program [13]. The detailed computational procedure to obtain defect formation energies can be found in Refs. [9] and [10]. In these studies, the stable point defects were determined as a function of Fermi level and oxygen chemical potential without a local electroneutrality constraint as would be applicable to the interfacial regions between the high-k oxide and silicon. In the bulk regions of the oxides, charges from positively charged defects have to be balanced by charges from negatively charged defects to maintain charge neutrality. This condition can be fulfilled at least a few atomic layers away from interfacial region where the bulk form of material is resumed and hence a higher energy barrier is present to carriers in the channel region. The charge neutrality condition is given by

$$\text{net charge} = \sum_i q_i c_i = 0,$$

where $q_i$ is the charge associated with a particular defect $i$ and $c_i$ is its concentration. Under equilibrium con-
ditions, the concentration of a point defect is given by

\[ c_i = N_{\text{site}} \exp \left( -\frac{E_i}{k_B T} \right), \]

where \( N_{\text{site}} \) is the number of lattice sites on which the defect can occur (per unit volume), \( E_i \) is the formation energy of the point defect, \( k_B \) is the Boltzmann constant, and \( T \) is the growth temperature of the material. The formation energies for native point defects are a function of Fermi level and chemical potentials, and their values for HfO\(_2\), ZrO\(_2\), and Y\(_2\)O\(_3\) have been reported in Refs. [9] and [10]. It is noted that although a thermodynamic equilibrium condition is assumed, the formation energies can serve as a good indicator as to which defects are more likely to form and which material is more prone to the formation of certain type of defects, even when the equilibrium condition is not completely reached. The supercell approach used in the calculations introduces artificial interactions between charge defects and their image charges [14]. In this study, the formation energies for charged defects are corrected for the image charge interactions using the leading term (\( L^{-1/2} \) term where \( L \) is the supercell size) in the Makov–Payne correction scheme [14]. The values for the image charge corrections for different charge states in HfO\(_2\) and ZrO\(_2\) were reported in Ref. [10]. The image charge corrections in YO\(_2\) (\( k = 16 \)) and LaO\(_2\) (\( k = 25 \)) are 0.12 eV and 0.07 eV, respectively for \( \pm 1 \) charge defects and they scale proportionally with \( q^2 \) for \( \pm q \) charge defects. The possible oxygen chemical potential is bound by the stability of the compounds with respect to the pure metal and molecular oxygen [9, 10]. The allowable range for oxygen chemical potential in HfO\(_2\) or ZrO\(_2\) is given as

\[ \mu^0_o + \frac{1}{2} \Delta E_i^{\text{M(O)}} < \mu^0_o < \mu^0_o, \]

where \( \mu^0_o \) is the chemical potential for oxygen in MO (\( M = \text{Hf} \) or Zr), \( \mu^0_o \) is the energy of an oxygen atom in O\(_2\) gas, and \( \Delta E_i^{\text{M(O)}} \) is the formation enthalpy of MO. Similarly the range for oxygen chemical potential in M\(_2\)O\(_3\) (\( M = \text{Y} \) or La) is given as

\[ \mu^0_o + \frac{1}{2} \Delta E_i^{\text{M(O)}} < \mu^0_{M(O)} < \mu^0_o. \]

The formation energies for the neutral oxygen vacancy (\( V_o \)) and oxygen interstitial (\( O_i \)) in these four oxides are shown in Table 1 under oxidation condition.

The large concentration of pre-existing bulk defects that is usually present in high-\( k \) oxides can trap electrons during device operation [2]. The shift in the threshold voltage due to trapped charges can be estimated as \( \Delta V_\text{th} = \frac{Q_{\text{tot}}}{C_{\text{ox}}} \), where \( Q_{\text{tot}} \) is the total trapped charge concentration, \( t_{\text{ox}} \) is the physical thickness of the high-\( k \) oxide and \( C_{\text{ox}} \) is the gate oxide capacitance per unit area. For a high-\( k \) gate oxide with a dielectric constant of \( k = 20 \) and \( t_{\text{ox}} = 4 \) nm (corresponding to an equivalent oxide thickness of less than 1 nm), the defect concentration needs to be approximately \( 7 \times 10^{12} \) cm\(^{-3} \) to cause a 10 mV shift in the threshold voltage, assuming that all defects are fully charged.

It is known that the defect concentration cannot be significantly reduced by annealing after deposition of the gate dielectric, and is largely determined by the source/drain activation anneal that is carried out at about 1000 °C [2]. Thus, \( T = 1300 \) K is used to calculate the defect concentrations. We have considered all the native point defects, including oxygen and metal vacancies, oxygen and metal interstitials, and oxygen and metal antisites. The negative charge states for oxygen vacancies are also considered [7].

### 3 Results and discussion

The concentrations of native point defects in bulk HfO\(_2\) are shown in Fig. 1a for those defects that reach a concentration greater than \( 10^5 \) cm\(^{-3} \). From the figure, the first observation is that the dominant defects are all oxygen-related defects. When the local electroneutrality constraint is not imposed, different types of defects can become dominant depending on the Fermi level and oxygen chemical potential [10]. In general, positively charged defects can only dominate at the Fermi level near the valence band as their formation energies increase with the Fermi level, while negatively charged defects usually dominate at a high Fermi level as their formation energies decrease with the Fermi level. When the local electroneutrality is constrained, the Fermi level is no longer an independent variable, but it has to equilibrate to a value which keeps the average charges of all the defects neutral. For instance, under oxidation condition in HfO\(_2\) without the local electroneutrality constraint, the formation energies for metal vacancies become negative over a large range of the Fermi level near the conduction band, leading to a substantial trend to form such defects. At the Fermi level where metal vacancies are dominant, there are no compensating defects with positive charges. To satisfy the charge neutrality requirement, the Fermi level has to move closer to the valence band where charged oxygen interstitials eventually dominate over charged metal vacancies and at the same time positively charged oxygen vacancies become the charge compensating defects.

In HfO\(_2\), the dominant charged defects are positively charged oxygen vacancies (\( V_o^{2+} \)) and negatively charged oxygen interstitials (\( O_i^- \)). Their concentrations are almost independent of the oxygen partial pressure, indicating that they form as oxygen Frenkel pairs in HfO\(_2\). The concentrations for these charged defects are too low (<\( 10^{12} \) cm\(^{-3} \)) to have any significant effects on device operation. On the other hand, the dominant neutral defects are oxygen vacancies under reducing conditions and oxygen interstitials under oxidation conditions. As the defect concentrations are determined by the source/drain activation anneal, which corresponds to a reducing condition, neutral oxygen va-

| Table 1 Formation energies in eV for \( V_o \) and \( O_i \) under oxidation condition (\( \mu^0_o = \mu^0_{O_2} \)). |
| --- | --- | --- | --- | --- |
| HfO\(_2\) | ZrO\(_2\) | Y\(_2\)O\(_3\) | LaO\(_2\) |
| \( V_o \) | 6.63 | 6.15 | 6.92 | 6.64 |
| \( O_i \) | 1.58 | 1.31 | 0.48 | 0.47 |

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vacancies are expected to be the most dominant native point defects. This is in agreement with Ref. [2] where it has been argued that the vacancies are initially neutral since no strong threshold voltage shift with increasing oxide thickness is observed. Although the coexistence of an equal amount of positively and negatively charged defects would also be consistent with that observation, this is not the case in HfO$_2$ as the concentrations of all charged defects are too low. The concentrations of dominant defects as a function of temperature in HfO$_2$ under reducing conditions are shown in Fig. 2. It can be seen that the defect concentrations can be lowered dramatically when the temperature is decreased. It should be noted that the following assumptions are used to calculate the defect concentrations: (1) Eq. (2) does not account for the formation entropy of the point defect, which could increase the concentrations by two to three orders of magnitude [15]. (2) No corrections were applied to correct for band gap errors using DFT as it is still an ongoing debate on how to apply such corrections [16, 17]. Recently, various hybrid functionals have been employed to study defects in HfO$_2$ [6, 7]. Although these methods produce a band gap value closer to experimental measurement, they are not widely adopted in the defect energy calculations and thus further investigation is needed. (3) An equilibrium condition is assumed.

The concentrations of point defects in ZrO$_2$ are shown in Fig. 1b. The types of dominant defects are the same as those in HfO$_2$. However, the concentrations of neutral oxygen vacancies and oxygen interstitials in ZrO$_2$ are about two orders of magnitude higher than those in HfO$_2$ under the same oxygen chemical potential. This is consistent with the conclusion that HfO$_2$ is less prone to the formation of oxygen point defects than ZrO$_2$ [10].

The concentrations of point defects in Y$_2$O$_3$ and La$_2$O$_3$ are shown in Fig. 1c and d, respectively. The dominant defects are also oxygen-related defects. The concentrations of V$_{0i}^{+}$ and O$_{i}^{2-}$ are not entirely independent of the oxygen chemical potential due to the existence of V$_{Oi}^{0}$, as no negative-U behavior for oxygen vacancies in Y$_2$O$_3$ and La$_2$O$_3$ is observed. The concentration of V$_{0i}$ can be larger than that of V$_{Oi}$ under reducing condition, thus becoming the dominant defect to compensate the charges from O$_{i}^{2-}$. When two V$_{0i}$ compensate for one O$_{i}^{2-}$, the concentrations of V$_{0i}$ and O$_{i}^{2-}$ become dependent on the oxygen partial pressure. Compared to HfO$_2$ and ZrO$_2$, the concentrations of V$_{0i}$ and O$_{i}^{2-}$ are higher in Y$_2$O$_3$ and La$_2$O$_3$. Thus besides the neutral oxygen vacancies that can act as electron traps in Y$_2$O$_3$ and La$_2$O$_3$, charged oxygen vacancies could also be responsible for electron trapping in these materials. The concentration of neutral oxygen interstitials is high in Y$_2$O$_3$ and La$_2$O$_3$ under oxidation conditions due to the existence of structural anion vacancies in the cubic bixbyite structures.

References