Effects of barium incorporation into HfO$_2$ gate dielectrics on reduction in charged defects: First-principles study

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Reducing the number of charged defects in the gate insulating oxides is an essential task to improve the electrical properties of field-effect transistors. Our comprehensive study using first-principles calculations revealed that incorporating Ba atoms into HfO$_2$ can markedly decrease the number of charges associated with oxygen vacancies (V$_{O}$). This is attributed to the strong coupling of a Ba atom substituted for Hf (Ba$_{Hf}$) with V$_{O}$, rendering the complex defect Ba$_{Hf}$V$_{O}$ stable in the charge-neutral state. © 2009 American Institute of Physics. [DOI: 10.1063/1.3070534]

HfO$_2$ is a high permittivity (high-$\kappa$) gate insulating oxide used for field-effect transistors (FETs).$^{1,2}$ One serious problem with high-$\kappa$ oxides is their high concentration of charged defects, which are often called fixed charges. The neutral oxygen vacancy V$_{O}$ forms a doubly occupied state in the band gap near the conduction band minimum in HfO$_2$,$^{3,4}$ and removal of the two electrons can satisfy the closed shell, rendering the V$_{O}$ a stable charged defect. Such charged defects, however, degrade the mobility of channel current carriers due to Coulomb scattering. Moreover, the positively charged defects attract negative carriers, acting as electron trap sites in the gate oxide. This is problematic because the trapping and detrapping of electrons at V$_{O}$ cause instability of the threshold voltage during FET operation. Thus, the reduction in the charged defects is a crucial part of developing high-$\kappa$ gate oxides.

Incorporating foreign atoms into HfO$_2$ is one possible solution to control the number of fixed charges. Previous studies suggested that N incorporation into HfO$_2$ is effective for controlling the number of fixed charges$^{5}$ and the suppression of the electron traps.$^{6,9}$ Effects of doping with F,$^{7,10,11}$ Al,$^{12}$ and La (Ref. 13) into HfO$_2$ have also been studied elsewhere. Very recently, Mg incorporation was recognized as a promising technique to minimize the positive charges associated with V$_{O}^+_2$ in HfO$_2$. Many other species have been incorporated into HfO$_2$, yet the scope of such works has been mainly focused on the dielectric properties, and effects of impurities on the reliability of the gate insulating oxide are still unknown.

In this letter, we report an extensive study on the effect of Ba incorporation into HfO$_2$ using first-principles total energy calculations. Our computational results revealed that the complex defect of Ba at a Hf site, Ba$_{Hf}$, has been mainly focused on the dielectric properties, and effects of Ba-related defects with charge, Q, in HfO$_2$, namely, a single oxygen vacancy at threefold and fourfold oxygen sites ($V_{O3}^+$ and $V_{O4}^+$) (Q=0, +1, and +2), a Ba atom substituting for Hf (Ba$_{Hf}$) (Q=−2, −1, 0, +1, and 0), Ba$_{Hf}$ coupled with an oxygen vacancy at threefold and fourfold oxygen sites ($[Ba_{Hf}V_{O3}]^0$ and $[Ba_{Hf}V_{O4}]^0$) (Q=−2, −1, 0, +1, and +2), and both $V_{O3}$ and $V_{O4}$ ($[Ba_{Hf}V_{O3}V_{O4}]^0$ (Q=−2, −1, 0, +1, and +2). Compensating background charge was introduced for the charged defects to avoid divergence of the total energy without any corrections afterward. The atomic positions were relaxed until the total energy difference was converged within 0.001 eV, which results in having the residual forces below 0.03 eV/Å.

The stability of these defects was compared in terms of the formation energy defined by

\[ E_f(X^Q) = E_{tot}(X^Q) - E_{tot}(\text{bulk}) - \sum_i n_i \mu_i + Q(\varepsilon_F + \varepsilon_v + \Delta V) + E_{corr}, \]  

where $E_{tot}(X^Q)$ and $E_{tot}(\text{bulk})$ are the total energy of a defect with charge $Q$ and the bulk HfO$_2$, which were given by our DFT calculations. $n_i$ and $\mu_i$ are the number of atoms deviating from the perfect crystal and the chemical potential of each species ($i=$O, Hf, or Ba), respectively. $\varepsilon_F$ is the Fermi energy referenced with the valence band maximum $\varepsilon_v$ of bulk HfO$_2$. $\Delta V$ is the correction to $\varepsilon_v$ for the shift in the electrostatic potential due to the introduction of the defects into the supercell with respect to that in the bulk HfO$_2$, which we found is of the order of 0.18 eV at a maximum. $E_{corr}$ is another correction to $\varepsilon_v$ due to the special k-point sampling for the shallow acceptor (Ba$_{Hf}$ in our case): the

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energy difference between the top of the valence band at Γ and the other k-points sampled in our calculations, which is about −0.04 eV for BaHf. We set χ_{O3} to the condition where a bulk Si precipitates in SiO2; i.e., χ_{O3}=(χ_{total}(SiO2) − μ_{Si}[bulk])/2 because we are interested in HfO2 deposited on a Si substrate. Here, the total energy of SiO2, χ_{total}(SiO2), was obtained from a nine-atom cell for α-quartz, and the chemical potential of Si in a bulk Si, μ_{Si}[bulk], was calculated using the two-atom cell for diamond structure, which gives χ_{O3} = −4.8 eV as referenced from a half of the total energy of a single oxygen molecule. The chemical potential of Ba was then given by the equilibrium condition, μ_{Ba} = χ_{total}(BaO)−μ_{O}, where χ_{total}(BaO) was calculated from a two-atom unit cell of the rocksalt structure.

Figure 1 shows formation energies for the intrinsic and Ba-related defects. Here, ε_{F} is measured from the valence band maximum, and the upper limit of ε_{F} corresponds to the conduction band minimum of HfO2−V_{O3} and Ba_{Hf}−V_{O3} predicted in low and high ε_{F} conditions, respectively. This is the same situation as the Mg-related defects in HfO2, where M_{G}Hf^{2+} predominates at a high ε_{F}. However, the formation energy of Ba_{Hf}^{2+} is higher than that of M_{G}Hf^{2+} by 1.8 eV. This is reasonable because the ionic radii of Mg (0.72 Å) and Hf (0.83 Å) are comparable, while that of Ba (1.42 Å) is very large compared to them. Thus, substituting Ba for Hf introduces large strains around the Ba, destabilizing Ba_{Hf}^{2+}. In contrast, the formation energy of [Ba_{Hf}V_{O3}]^{0} (2.7 eV) is relatively low and comparable to that of [M_{G}HfV_{O3}]^{0} (2.2 eV) reported in Ref. 14.

The binding energy gained by the chemical reaction Ba_{Hf}^{2+}V_{O3}^{2+} → [Ba_{Hf}V_{O3}]^{0} is calculated from E_{b}([Ba_{Hf}V_{O3}]^{0}) = E_{b}(Ba_{Hf}^{2+})+E_{b}(V_{O3}^{2+})−E_{b}([Ba_{Hf}V_{O3}]^{0}) which we found is very large: 3.0 eV. This clearly indicates that a Ba atom is spontaneously coupled with V_{O3} forming [Ba_{Hf}V_{O3}]^{0}, as incorporated into HfO2. Another binding energy gained by the reaction [Ba_{Hf}V_{O3}]^{0} + V_{O3} → [Ba_{Hf}V_{O3}]^{2+} (1.4 eV) is much smaller than E_{b}(Ba_{Hf}V_{O3})^{0}, and thus the concentration of [Ba_{Hf}(V_{O3})]^{2+} is not significantly increased over [Ba_{Hf}V_{O3}]^{0}.

According to our analysis on the relative concentrations of these defects, [Ba_{Hf}V_{O3}]^{0} predominates among V_{O3}^{2+}, [Ba_{Hf}V_{O3}]^{0}, and [Ba_{Hf}(V_{O3})]^{2+} at any temperature while the sample is cooled down after the annealing at 1000 °C. Detailed procedure for this analysis is presented in our previous paper.14

The great stability of [Ba_{Hf}V_{O3}]^{0} is partly due to the existence of an extra space at V_{O3}, which comforts strains introduced by substituting Ba for Hf. In Ba_{Hf}^{2+}O atoms were found to relax away from the Ba atom by 16% due to the large ionic radius of Ba. This strain is somewhat released by the removal of an O atom from the vicinity of BaHf. The Ba atom, then relaxes toward the V_{O3} site, seeking an open space to comfort the strain, rendering the [Ba_{Hf}V_{O3}]^{0} a stable defect (Fig. 2). The relaxation energy was found to be very large (8.4 eV) in comparison with that of V_{O3}^{2+} (2.6 eV). In fact, the Ba−V_{O3} distance (1.4 Å) is much shorter than a Ba−O distance (2.7 Å). This is consistent with the previous experimental report; i.e., the Ba atom can readily migrate into HfO2 when a BaO layer is deposited on HfO2 in spite of the sizable difference in the ionic radii between Ba and Hf.20

Attractive Coulomb interactions between the negatively charged Ba^{2−} and the positively charged V_{O3}^{2+} are also relevant to the stability of [Ba_{Hf}V_{O3}]^{0}. Substituting the divalent Ba for the tetravalent Hf induces two holes at the valence band maximum. A closed shell structure is then achieved by adding two extra electrons, which are supplied by introducing a neutral oxygen vacancy. The two electrons are, therefore, transferred from V_{O3} to Ba_{Hf}^{2−}, causing the attractive interactions between Ba_{Hf}^{2−} and V_{O3}^{2+} in the neutral complex [Ba_{Hf}V_{O3}]^{0}. This kind of electron counting concept is surprisingly valid in an ionic compound such as HfO2. It is interesting to notice that the formation energy of [Ba_{Hf}V_{O3}]^{0} is higher than that of [Ba_{Hf}V_{O3}]^{0} by 2.0 eV (Fig. 1). We found that the Ba−V_{O3} distance (1.9 Å) is much longer than Ba−O distance (1.4 Å) probably due to the restrictions on the local geometry around V_{O3}. Hence, the energy gain from the attractive Coulomb interaction between the two constituents is limited in [Ba_{Hf}V_{O3}]^{0}. The transition level of the charge states in Ba_{Hf}V_{O3} from 0 to +2 (ε_{F}=3.7 eV), which is often called a thermodynamic transition level, ε(0)−2, is much higher than ε(0) of V_{O3} (ε_{F}=2.9 eV) as shown in Fig. 1. Here,
This is reflected in the partial charge densities corresponding for Hf, destabilizing the electrons trapped at the vacancy. The formation of the neutral complex \( \text{BaHfO}_3 \) insulator brings certain advantages to the quality of the Hf-based gate compared to Mg incorporation in terms of the reduction in the fixed charges, thanks to the suppression of the electron traps due to the formation of \( \text{BaHfO}_3 \). This indicates that the defect sites \( \text{BaHfO}_3 \) and \( \text{MgHfO}_3 \) correspond to the occupation of two \( \text{BaHfO}_3 \) and \( \text{MgHfO}_3 \), respectively. It is understood that some electrons at the vacancy site leave away from the Ba to approach a Hf atom at a second nearest neighbor site to decrease the Coulomb energy of the system [Fig. 3(b)]. This delocalizes the occupied electrons, causing the shallower level in \( \text{BaHfO}_3 \) than in \( \text{V}_{\text{O3}}^0 \).

Our theoretical analysis suggests that Ba incorporation brings certain advantages to the quality of the Hf-based gate insulator. One is reduction in the fixed charges, thanks to the formation of the neutral complex \( \text{BaHfO}_3 \), thereby reducing the Coulomb scattering of the channel current carriers. The other is the suppression of the electron traps due to the formation of a shallow level which allows trapped electrons released back to the electrode, inhibiting the threshold voltage instability. Moreover, Ba incorporation is even more promising than Mg incorporation in terms of the reduction in the charged defects because the binding energy gained by the reaction \( \text{BaHf}^{2+} + \text{V}_{\text{O3}}^2 \rightarrow [\text{BaHfO}_3]^0 \) (3.0 eV) is much larger than that gained by \( \text{Mg}^{2+} + \text{V}_{\text{O3}}^2 \rightarrow [\text{MgHfO}_3]^0 \) (1.6 eV), indicating that Ba incorporation into \( \text{HfO}_2 \) is more promoted than the Mg incorporation. Therefore, Ba incorporation is a very efficient way to reduce the fixed charges associated with \( \text{V}_{\text{O3}}^2 \).

In summary, effects of Ba incorporation into \( \text{HfO}_2 \) have been extensively studied. Our computational results suggest that Ba atoms are strongly coupled with oxygen vacancies, neutralizing the defect sites. This is beneficial for the improvement of the quality of the high-\( \kappa \) oxide.

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15E. Cockayne, J. Appl. Phys. 103, 084103 (2008), and references therein.
19The computational band gap (3.9 eV) underestimates the experimental value [5.7 eV (Ref. 3)] due to the common problem of LDA. Our conclusion, however, is not significantly affected by this issue because all the thermodynamic transition levels considered in this work are in the band gap (Fig. 1) and the corresponding wave functions are located around the defect sites (Fig. 3).