Origin of high solubility of silicon in La$_2$O$_3$:
A first-principles study

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Origin of high solubility of silicon in La$_2$O$_3$: A first-principles study

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The solubility of silicon in high-permittivity (high-$\kappa$) oxides significantly affects the performance of field-effect transistors. Our comparative study of silicon impurities in La$_2$O$_3$ and HfO$_2$ reveals that the stability of silicon at substitutional sites strongly depends on its coordination number. When substituted for lanthanum, a silicon atom fits comfortably in La$_2$O$_3$, thanks to the formation of a SiO$_4$ tetrahedral structure. In addition, the substitutional silicon acts as a donor impurity in La$_2$O$_3$, increasing oxygen content in the oxide. This contributes to absorbing silicon and oxygen from the interface region, leading to the formation of lanthanum silicate at the La$_2$O$_3$/silicon interface.

The continuous downscaling of field-effect transistors (FETs) has led to the use of extremely thin SiO$_2$ films as gate insulators, giving rise to considerable problems with leakage currents. Consequently, over the past decades, a great deal of effort has been made to replace SiO$_2$ with a high-permittivity (high-$\kappa$) oxide in order to achieve a large capacitance within a sufficiently large oxide thickness.$^{1,2}$

However, this means abandoning the excellent SiO$_2$/silicon interface, which has played an important role in the great developments of the silicon technology, and moving to an alternative oxide/silicon interface. Extensive studies on high-$\kappa$ oxides such as HfO$_2$ have shown that this is a very challenging task due to the undesirable oxidation of silicon substrates during fabrication processes. The formation of silicon oxide SiO$_2$ at the HfO$_2$/silicon interface substantially decreases the overall dielectric constant of the oxide film and must be avoided in order to make use of the advantages of the high-$\kappa$ oxides.

Recently, La$_2$O$_3$ has attracted a great deal of attention for numerous reasons, including its high dielectric constant (18.8–27 eV) (Refs. 3–5) and wide band gap (5.4–6.4 eV).$^{6,8}$ Moreover, silicon atoms readily dissolve in La$_2$O$_3$ to form silicate La$_2$(1-x)Si$_{3x+1}$O$_{3x}$, which allows direct contact between the high-$\kappa$ layer and a silicon substrate without the formation of a SiO$_2$ layer. However, little is known concerning the differences in the properties of HfO$_2$/silicon and La$_2$O$_3$/silicon. A clarification of this aspect is crucial for developing high-$\kappa$-based FETs.

In this letter, we report on a theoretical study of silicon stability in La$_2$O$_3$ and HfO$_2$. According to our model, the high solubility of silicon in La$_2$O$_3$ is attributed to the formation of a tetrahedral structure of SiO$_4$ and its charge state.

Our first-principles calculations are based on the density-functional theory (DFT) within the local-density approximation (LDA) using the projector augmented wave pseudopotentials as implemented in the VASP code.$^{15,16}$ The valence configurations of the pseudopotentials are 5s$^2$5p$^6$5d$^1$6s$^2$ for La, 5p$^6$5d$^4$6s$^2$ for Hf, 3s$^2$3p$^2$ for Si, and 2s$^2$2p$^4$ for O. Energy cutoff for the plane-wave basis set expansion was set 500 eV. A Monkhorst–Pack k-point set of 6x6x6 was used both for a five-atom cell of hexagonal La$_2$O$_3$ and a 12-atom cell of monoclinic HfO$_2$. Optimized lattice constants of these oxides are shown in Table I. These unit cells were extended to 50-atom and 96-atom supercells to construct model structures for defects in La$_2$O$_3$ and HfO$_2$, respectively.

We have explored various charge states of substitutional silicon in La$_2$O$_3$ and HfO$_2$: a silicon substituted for lanthanum Si$_{La}^{Q}$ ($Q$=0, +1, and +2) and for hafnium Si$_{Hf}^{Q}$ ($Q$=−1, 0, and +1). Native defects such as oxygen vacancies V$_O^{Q}$ ($Q$=+2) and oxygen interstitials O$_i^{Q}$ ($Q$=−2) are also investigated for comparison. Here, V$_O$ and O$_i$ are introduced at fourfold oxygen site and sixfold interstitial site in La$_2$O$_3$, respectively. In HfO$_2$, both the defects are at threefold sites. Compensating background charge was introduced for the charged defects to avoid divergence of the total energy, and no subsequent corrections were performed. The atomic positions were relaxed until the total energy difference converges to within 0.001 eV, which results in residual forces below 0.06 and 0.03 eV/Å for La$_2$O$_3$ and HfO$_2$, respectively. Here, the volumes of the supercells were also relaxed for Si$_{La}$ and Si$_{Hf}$ to take account of the shorter bond length of Si–O compared to La–O and Hf–O.

In Figs. 1(a) and 1(b), the density of states (DOS) for Si$_{La}^{Q}$ and Si$_{Hf}^{Q}$ are shown with partial charge densities corresponding to the Si–O bonding states. A silicon atom is coordinated with four and six oxygen atoms in La$_2$O$_3$ and HfO$_2$, respectively. This indicates that silicon is more comfortable

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<td>3.88</td>
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$^a$Reference 17.
$^b$Reference 18.
in La$_2$O$_3$ than in HfO$_2$ due to the formation of the stable tetrahedral structure SiO$_2$ shown in Fig. 1(a). Each lanthanum atom is coordinated with seven oxygen atoms (four fourfold and three sixfold) in a perfect crystal of La$_2$O$_3$. Substituting a silicon for lanthanum causes relaxations of the fourfold oxygen atoms toward Si forming the tetrahedral structure. The sixfold oxygen atoms do not participate in the formation of Si–O bonds but, instead, create fivefold oxygen sites at locations distant from Si. The inward and outward relaxations were found to be as much as 30%. In contrast, such large outward relaxations do not occur in HfO$_2$. Each hafnium atom is also sevenfold in a perfect crystal of monoclinic HfO$_2$, yet the concentration of oxygen in HfO$_2$ is 6.04 × 10$^{22}$ cm$^{-3}$, which is much higher than that in La$_2$O$_3$ (3.86 × 10$^{22}$ cm$^{-3}$), and thus, the relaxation is limited for oxygen in the highly packed HfO$_2$. This leads to the different bonding structures around Si in La$_2$O$_3$ and HfO$_2$.

In addition, Si$_{La}$ is a donor-type impurity as indicated by the highest occupied state located at the conduction band minimum [Fig. 1(a)]. This is reasonable in view of the fact that replacing a trivalent lanthanum by a tetravalent silicon donates an extra electron at the conduction band minimum. Electrons occupying such a high-lying state in a wide gap oxide are unstable, and acceptor-type defects are spontaneously formed to accommodate these electrons near the valence band maximum. An oxygen interstitial (Oi) is the most plausible acceptor in La$_2$O$_3$. Hence, substituting a silicon for lanthanum results in the formation of Oi. This scenario is schematically illustrated in Fig. 2.

The above discussion leads to an important finding: substituting Si for La would cause an increase in the oxygen content in La$_2$O$_3$. This explains the formation of the silicate La$_{2(1-x)}$Si$_{3x}$O$_3$ at the La$_2$O$_3$/Si interface. Silicon oxide SiO$_x$ is readily absorbed by La$_2$O$_3$ as soon as it is formed at the interface because Si$_{La}$ is highly stable in La$_2$O$_3$ and acts as a donor-type impurity, which promotes oxygen diffusion from SiO$_2$ to La$_2$O$_3$. This is not the case at the HfO$_2$/silicon interface. A silicon atom substituting for hafnium (Si$_{Hf}$) is found to be unstable due to the incomplete formation of the stable fourfold structure. In fact, the silicon atom is coordinated with six oxygen atoms as shown in Fig. 1(b). Moreover, Si$_{Hf}$ is not a donor-type impurity because Si and Hf are isovalent. Thus, neither silicon nor oxygen is absorbed in HfO$_2$, causing precipitation of SiO$_2$ at the HfO$_2$/Si interface.

To analyze the relative stabilities of substitutional silicon in La$_2$O$_3$ and HfO$_2$, we computed the formation energy of Si$_{La}$ and Si$_{Hf}$ and compared it to that of the native defects, $V_0$ and O$_i$ in each oxide,

$$E_f(X^O) = E_{tot}(X^O) - E_{tot}(bulk) - \sum_i n_i \mu_i + Q \varepsilon_F,$$

where $E_{tot}(X^O)$ and $E_{tot}(bulk)$ are respectively the total energy of a defect with charge $Q$ and that of bulk La$_2$O$_3$ or HfO$_2$ based on the DFT calculations. $n_i$ is the number of atoms added to the perfect crystal. $\varepsilon_F$ is the Fermi energy with respect to the valence band maximum $\varepsilon_v$ of the bulk system. $\mu_i$ is the chemical potential of each species ($i=$La, Hf, Si, or O). $\mu_{Si}$ was estimated from the total energy of bulk silicon using a two-atom cell of diamond structure. $\mu_{O}$ is set to reflect the condition at a SiO$_2$/Si interface: $\mu_{O} = (E_{tot}[SiO_2]-\mu_{Si})/2$, which corresponds to the situation where SiO$_2$ is present at the high-$\alpha$ oxide/silicon interface. Here, the total energy of SiO$_2$, $E_{tot}[SiO_2]$, was obtained from a nine-atom cell for $\alpha$-quartz, which gives $\mu_{O} = -4.8$ eV with respect to a half of the total energy of a single oxygen molecule. The chemical potentials of La and Hf were then given by the equilibrium conditions, $\mu_{La} = (E_{tot}[La_2O_3] - 3 \mu_{O})/2$ and $\mu_{Hf} = E_{tot}[HfO_2] - 2 \mu_{O}$.

Figures 3(a) and 3(b) show the formation energies of the.
defects in La$_2$O$_3$ and HfO$_2$, respectively. The upper limit of $\varepsilon_F$ corresponds to the conduction band minimum of each oxide. Here, only the predominant charge state, which corresponds to the slope of each line, is shown for Si$_{La}$ and Si$_{Hf}$. Si$_{La}$ is positively charged for a wide range of $\varepsilon_F$, indicating a donor-type impurity, while Si$_{Hf}$ is neutral over the entire range of $\varepsilon_F$. This difference in the stable charge state is the key to understanding the high solubility of silicon oxides in La$_2$O$_3$.

The concentration of a defect, $C(X^Q)$, is calculated from its formation energy as

$$C(X^Q) = N_{\text{sites}} \exp \left( \frac{-E_f(X^Q)}{k_B T} \right),$$

(2)

where $N_{\text{sites}}$ is the number of sites in the lattice per supercell in which the defect is formed, $k_B$ is the Boltzmann’s constant, and $T$ is the temperature. In the intrinsic case where silicon impurities are absent, the charge neutrality condition is satisfied when the number of $V^0_{O_2}$ and $O^{2-}$ are balanced, i.e., $C(V^0_{O_2}) = C(O^{2-})$, which yields $\varepsilon_F = 2.9$ eV for La$_2$O$_3$ and $\varepsilon_F = 3.0$ eV for HfO$_2$. These values correspond to the Fermi levels at which the two lines for $V^0_{O_2}$ and $O^{2-}$ intersect in Figs. 3(a) and 3(b) and are interpreted as the intrinsic Fermi levels.

The situation is dramatically changed when a silicon is substituted for lanthanum in La$_2$O$_3$; the countercharge of O$_{La}$ is twice that of O$_{La}$, is very stable and predominates around the intrinsic Fermi level [Fig. 3(a)]. Thus, charge neutrality is satisfied when the number of Si$_{La}$ is twice that of O$_{La}$, i.e., $2C(Si_{La}^+) = C(O_{La}^{2-})$, which yields $\varepsilon_F = 3.2$ eV. This value virtually corresponds to the Fermi level at which the two lines for O$_{La}^{2-}$ and Si$_{La}^+$ intersect in Fig. 3(a). Importantly, this extrinsic Fermi level is higher than the intrinsic Fermi level by 0.3 eV. The upward shift of the Fermi level decreases the formation energy of O$_{La}^{2-}$ [Fig. 3(a)] and thereby increases the oxygen content in La$_2$O$_3$. According to Eq. (2), the concentration of O$_{La}^{2-}$ is raised by four orders of magnitude in cm$^{-2}$ at 500 °C due to the formation of Si$_{La}^+$. Therefore, the migration of silicon into La$_2$O$_3$ is accompanied by an increment of the oxygen concentration in La$_2$O$_3$. This moderately explains why La$_{2(1-x)}$Si$_{3x/2}$O$_3$ is readily formed at La$_2$O$_3$/Si. Note that the relatively low formation energy of Si$_{La}^+$ is significant because if Si$_{La}$ were not stable, it would not be a predominant positive charge and unable to shift the Fermi level.

On the other hand, the Fermi level is unchanged upon the formation of Si$_{Hf}$ because it is neutral and unable to shift the Fermi level [Fig. 3(b)]. The relatively high formation energy of Si$_{Hf}^+$ (2.0 eV) also discourages silicon diffusion into HfO$_2$. As a result, if SiO$_x$ are formed at the HfO$_2$/silicon interface, they tend to remain at the interface region without mixing with HfO$_2$.

This result leads to the conclusion that the stability of silicon and its charge state in a host oxide significantly affect the oxygen content in the oxide. In a trivalent oxide such as La$_2$O$_3$, the tetravalent Si atom acts as a donor when substituted for La, increasing the oxygen concentration in the oxide. On the contrary, a divalent cation would be an acceptor-type impurity in La$_2$O$_3$, decreasing the oxygen concentration. This concept is valid as long as the dopant impurity can comfortably fit into the cation site of the host material and is applicable to any oxides.

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