Origin of high solubility of silicon in La_2O_3: A first-principles study

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(Received 3 July 2010; accepted 28 October 2010; published online 17 November 2010)

The solubility of silicon in high-permittivity (high-κ) oxides significantly affects the performance of field-effect transistors. Our comparative study of silicon impurities in La_2O_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_2O_3, thanks to the formation of a SiO_4 tetrahedral structure. In addition, the substitutional silicon acts as a donor impurity in La_2O_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_2O_3/silicon interface. © *2010 American Institute of Physics*. [doi:10.1063/1.3517485]

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-κ) 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-κ 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_x 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-κ oxides.

Recently, La_2O_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_2O_3 to form silicate $La_{2(1-x)}Si_{3x/2}O_3$,[9–14] which allows direct contact between the high-κ layer and a silicon substrate without the formation of a SiO_x layer. However, little is known concerning the differences in the properties of HfO_2/silicon and La_2O_3/silicon. A clarification of this aspect is crucial for developing high-κ-based FETs.

In this letter, we report on a theoretical study of silicon stability in La_2O_3 and HfO_2. According to our model, the high solubility of silicon in La_2O_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, $5p^6 5d^2 6s^2$ 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 $6 \times 6 \times 6$ was used both for a five-atom cell of hexagonal La_2O_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_2O_3 and HfO_2, respectively.

We have explored various charge states of substitutional silicon in La_2O_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_2O_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_2O_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}^0 and Si_{Hf}^0 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_2O_3 and HfO_2, respectively. This indicates that silicon is more comfortable

TABLE I. Lattice constants for La_2O_3 and HfO_2 determined by LDA compared to experimental values.

	LDA	Experiment
La_2O_3		
a (Å)	3.88	3.9373[a]
c (Å)	5.96	6.1299[a]
HfO_2		
a (Å)	5.04	5.117[b]
b (Å)	5.11	5.175[b]
c (Å)	5.21	5.291[b]
β (°)	99.74	99.22[b]

[a]Reference 17.
[b]Reference 18.

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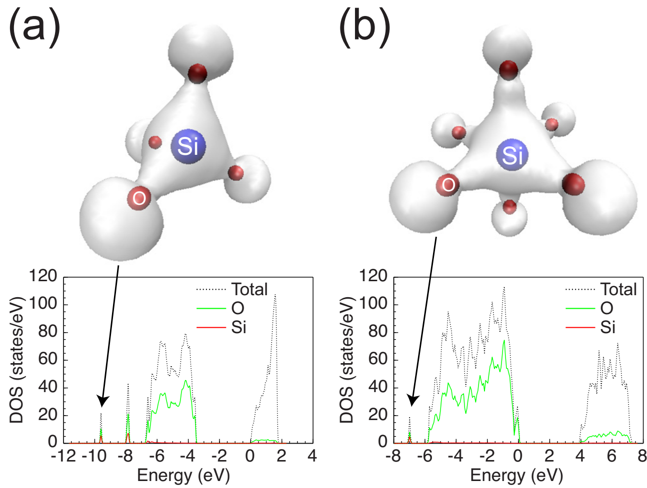

FIG. 1. (Color online) [(a) and (b)] Partial charge density corresponding to the bonding states of Si with coordinated oxygen atoms in (a) La_2O_3 and (b) HfO_2. The isosurfaces are at 0.05 electrons/Å^3. Total DOS and the projected (local) DOS for oxygen and silicon are also shown for (a) Si^0_{La} and (b) Si^0_{Hf} at the lower panel in each figure. For the local DOS, we use spheres of radii 1.312 and 0.82 Å for Si and O, respectively. The zero energy is at the highest occupied state.

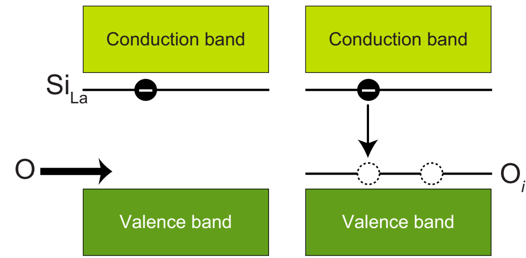

FIG. 2. (Color online) Schematic illustration of electron transfer from the donor level associated with the substitutional Si for La (Si_{La}) to an acceptor level associated with an oxygen interstitial (O_i).

in La_2O_3 than in HfO_2 due to the formation of the stable tetrahedral structure SiO_4 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_2O_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_2O_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_2O_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 (O_i) is the most plausible acceptor in La_2O_3. Hence, substituting a silicon for lanthanum results in the formation of O_i. 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_2O_3. This explains the formation of the silicate $La_{2(1-x)}Si_{3x/2}O_3$ at the La_2O_3/Si interface. Silicon oxide SiO_x is readily absorbed by La_2O_3 as soon as it is formed at the interface because Si_{La} is highly stable in La_2O_3 and acts as a donor-type impurity, which promotes oxygen diffusion from SiO_x to La_2O_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_x at the HfO_2/Si interface.

To analyze the relative stabilities of substitutional silicon in La_2O_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_O and O_i in each oxide,

$$E_f(X^Q) = E_{tot}(X^Q) - E_{tot}(\text{bulk}) - \sum_i n_i\mu_i + Q\varepsilon_F, \quad (1)$$

where $E_{tot}(X^Q)$ and $E_{tot}(\text{bulk})$ are respectively the total energy of a defect with charge Q and that of bulk La_2O_3 or HfO_2 based on the DFT calculations. n_i is the number of atoms added to the perfect crystal. ε_F is the Fermi energy with respect to the valence band maximum ε_v of the bulk system. μ_i is the chemical potential of each species (i=La, Hf, Si, or O). μ_{Si} was estimated from the total energy of bulk silicon using a two-atom cell of diamond structure. μ_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 are present at the high-κ oxide/silicon interface. Here, the total energy of SiO_2, $E_{tot}[SiO_2]$, was obtained from a nine-atom cell for α-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

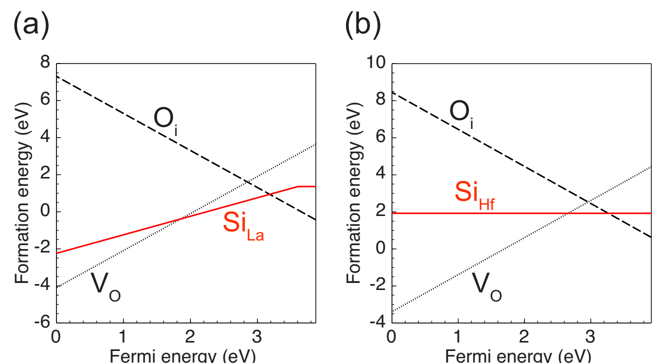

FIG. 3. (Color online) [(a) and (b)] Formation energies as a function of Fermi energy for (a) Si substituted for La (Si_{La}) and (b) Si substituted for Hf (Si_{Hf}). The formation energies of the positively charged oxygen vacancy (V_O^{+2}) and negatively charged oxygen interstitial (O_i^{-2}) are also shown in each figure. The slope of each line reflects the charge state of each defect.

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defects in La_2O_3 and HfO_2, respectively. The upper limit of ε_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 ε_F, indicating a donor-type impurity, while Si_{Hf} is neutral over the entire range of ε_F. This difference in the stable charge state is the key to understanding the high solubility of silicon oxides in La_2O_3.

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

$$C(X^Q) = N_{\text{sites}} \exp\left[-\frac{E_f(X^Q)}{k_B T}\right], \tag{2}$$

where N_{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_O^{+2} and O_i^{-2} are balanced, i.e., $C(V_O^{+2})=C(O_i^{-2})$, which yields $\varepsilon_F=2.9$ eV for La_2O_3 and $\varepsilon_F=3.0$ eV for HfO_2. These values correspond to the Fermi levels at which the two lines for V_O^{+2} and O_i^{-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_2O_3; the countercharge of O_i^{-2} is now Si_{La}^{+1} instead of V_O^{+2} because Si_{La}^{+1} is very stable and predominates around the intrinsic Fermi level [Fig. 3(a)]. Thus, charge neutrality is satisfied when the number of Si_{La}^{+1} is twice that of O_i^{-2}, i.e., $2C(Si_{La}^{+1})=C(O_i^{-2})$, which yields $\varepsilon_F=3.2$ eV. This value virtually corresponds to the Fermi level at which the two lines for O_i^{-2} and Si_{La}^{+1} 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_i^{-2} [Fig. 3(a)] and thereby increases the oxygen content in La_2O_3. According to Eq. (2), the concentration of O_i^{-2} is raised by four orders of magnitude in cm^{-3} at 500 °C due to the formation of Si_{La}^{+1}. Therefore, the migration of silicon into La_2O_3 is accompanied by an increment of the oxygen concentration in La_2O_3. This moderately explains why $La_{2(1-x)}Si_{3x/2}O_3$ is readily formed at La_2O_3/Si. Note that the relatively low formation energy of Si_{La}^{+1} is significant because if Si_{La}^{+1} were not stable, it would not be 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}^0 (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_2O_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_2O_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.

We would like to thank T. Chikyow, K. Ohmori, K. Yamada, T. Nakayama, and J. Robertson for fruitful discussions and advice. All of the calculations were performed on Hewlett-Packard clusters in the California NanoSystems Institute at UC Santa Barbara. This work was supported by the Japan Society for the Promotion of Science KAKENHI (Grant No. 21760030).

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