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Theoretical model for artificial structure modulation of HfO₂/SiOₓ/Si interface by deposition of a dopant material

Naoto Umezawa¹,²,a) and Kenji Shiraishi³

¹Environmental Remediation Materials Unit, National Institute for Materials Science, Ibaraki 305-0047, Japan
²PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan
³Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba 305-8571, Japan

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Realization of an abrupt HfO₂/Si interface without unintentional oxidation of the silicon substrate is a crucial task for the development of modern field-effect transistors. Here, we present a theoretical model which suggests that deposition of a dopant material on the HfO₂ layer turns it into an oxygen absorber, suppressing the formation of SiO₂ at the interface. Tantalum is predicted as an effective dopant in HfO₂ for this purpose. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.3689968]

The state-of-the-art field effect transistor (FET) consists of a thin-film oxide with a thickness of less than 10 nm that is sandwiched by a silicon substrate and a metallic electrode.¹,² It has recently been found that chemical reactions occurring at the bottom oxide/Si interface significantly affect the band alignment of the top metal/oxide interface.³ This finding strongly suggests that in order to understand the electronic and geometrical properties of a particular interface in a thin-film stack, effects taking place at other interfaces in the stack must be taken into consideration.

The stable nature of the SiO₂/Si interface has facilitated the rapid development of FET-based electrical devices. However, the recent requirement of replacing SiO₂ with a high permittivity (high-κ) oxide such as HfO₂ (Refs. 1 and 2) imposes a challenge on the interfacial design. It has been found that achieving an atomically abrupt interface between a high-κ oxide and silicon is extremely difficult due to undesired oxidation of the silicon substrate.⁴ The formation of a SiOₓ layer at the high-κ oxide/Si interface substantially decreases the permittivity of the oxide film, and a practical solution to this problem is still awaited.

When an oxide insulator is doped with donors, electrons are introduced at the conduction band minimum. However, the electron occupation of such a high-lying state is unfavorable in a wide-gap oxide, and acceptor-type defects are spontaneously formed in order to accommodate these electrons near the valence band maximum (see Fig. 1(a)). For example, tantalum can act as a donor-type impurity in HfO₂. Substituting a pentavalent tantalum cation for a tetravalent hafnium cation (TaHf) donates an extra electron to the lowest available state, namely the conduction band minimum.⁵ The band gap of HfO₂ (5.7 eV (Ref. 6)) is much wider than that found in semiconductors, thus these extra electrons can only be stabilized in lower energy levels. This acts as a driving force for the formation of acceptor-type defects such as oxygen interstitials (O_i).⁷,⁸ A neutral O_i generates an unoccupied state just above the valence band, which acts as an acceptor level and allows electron transfer from the donor level, leading to a closed-shell electronic structure as shown in Fig. 1(a). Here, one O_i is capable of accommodating two electrons supplied by two TaHf dopant cations. Rather surprisingly, this electron

FIG. 1. (Color online) Schematic illustrations of the effect of donor-type impurities in a wide-gap oxide. (a) Electrons occupying high-lying donor levels are in an energetically unstable situation. Therefore, acceptor-type defects are spontaneously formed to accommodate these electrons just above the valence band maximum. Electron transfer from the donor to acceptor level results in a closed-shell electronic structure, stabilizing the system. The left-hand panels depict structural geometries of impurities in HfO₂: substitutional tantalum for hafnium (TaHf) and interstitial oxygen (O_i) act as a donor and acceptor, respectively. The concentration of the acceptor-type defect O_i and thereby the oxygen content in HfO₂ are increased on doping with tantalum. (b) Atomic diffusion is driven by capping HfO₂/SiOₓ/Si with a layer of Ta₂O₅...c). The capping layer encourages the diffusion of tantalum into HfO₂, forming TaHf, which leads to scavenging of oxygen atoms from SiO₂ and hence the formation of O_i. This atomic diffusion reduces the thickness of the SiO₂ layer.

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*Author to whom correspondence should be addressed. Electronic mail: umezawa.naoto@nims.go.jp.

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and $b = \frac{1}{2}$ for a 12-atom unit cell of monoclinic HfO$_2$. The optimized formation of SiO$_2$ defect with charge $Q$ is now

to construct a model for the defects in HfO$_2$. In order to further understand this phenomenon, we have computed the concentration of tantalum (Ta$_{Hf}$) in HfO$_2$. Our first-principles calculations were based on density-functional theory (DFT) within the local-density approximation (LDA), using the projector augmented wave pseudopotentials as implemented in the VASP code.\textsuperscript{14,15} The valence configurations of the pseudo-potentials were 5$p^6$d$^5$ 6$s^2$ for tantalum, 5$p^6$d$^5$ 5$s^2$ for hafnium, and 2$s^2$ 2$p^3$ for oxygen. The energy cut-off for the plane-wave based expansion was set to 500 eV. A Monkhorst-Pack k-point set of 6 x 6 x 6 was used for a 12-atom unit cell of monoclinic HfO$_2$. The optimized lattice constants were $a = 5.04 \text{Å}$, $b = 5.11 \text{Å}$, $c = 5.21 \text{Å}$, and $\beta = 99.74^\circ$, which are in good agreement with the experimental values ($a^{expt} = 5.117 \text{Å}$, $b^{expt} = 5.175 \text{Å}$, $c^{expt} = 5.291 \text{Å}$, and $\beta = 99.22^\circ$ (Refs. 16 and 17)). A 96-atom supercell was used to construct a model for the defects in HfO$_2$. We have considered two charge states for Ta$_{Hf}$ ($Q = 0$ and +1). The oxygen vacancies $V_{O}^{+2}$ and oxygen interstitials $O_{i}^{-2}$ were also investigated in this work. Both native defects are placed at three-fold sites because they favor lower coordinations.\textsuperscript{18} Compensation of the background charge was introduced for the charged defects in order to avoid divergence of the total energy without any corrections afterwards. The atomic positions were relaxed until the total energy difference converged to within 0.001 eV, which results in residual forces below 0.03 eV/Å.

The formation energy of Ta$_{Hf}$ is the energy required to replace a hafnium cation by a tantalum cation in the oxide lattice

$$E_f(\text{Ta}_{Hf}^Q) = E_{tot}(\text{Ta}_{Hf}^Q) - E_{tot}(\text{bulk}) - \mu_{Ta} + \mu_{Hf} + Q\epsilon_F,$$  \hspace{1cm} (1)

where $E_{tot}(\text{Ta}_{Hf}^Q)$ and $E_{tot}(\text{bulk})$ are the total energies of the defect with charge $Q$ and of bulk HfO$_2$, respectively, which are given by our density-functional calculations. The quantities $\mu_{Ta}$ and $\mu_{Hf}$ are the chemical potentials of tantalum and hafnium which are estimated from an equilibrium condition in each oxide with the oxygen chemical potential at a Si/ SiO$_2$ interface,\textsuperscript{5} and $\epsilon_F$ is the Fermi energy with respect to the valence band maximum of bulk HfO$_2$. The formation energies of relevant dopants as well as the native defects are shown in Fig. S3.

The concentration of Ta$_{Hf}$ is then calculated from the formula

$$C(\text{Ta}_{Hf}^Q) = \frac{N_{sites}}{V_{cell}} e^{\frac{E_f}{k_B T}} + 1,$$  \hspace{1cm} (2)

where $N_{sites}$ is the number of available sites for the defect in supercell and $V_{cell}$ is the cell volume. $k_B$ is Boltzmann’s constant, and $T$ is set at the typical annealing temperature (1000°C) for the gate stack. The tantalum concentration is shown as a function of Fermi energy in Fig. 2, where the upper limit of $\epsilon_F$ corresponds to the conduction band minimum of HfO$_2$. The concentrations of the dominant native defects in HfO$_2$, positively charged oxygen vacancies $V_{O}^{+2}$ and negatively charged oxygen interstitials $O_{i}^{-2}$, are also shown in the figure. In the case without tantalum doping, the charge neutrality condition is satisfied when the concentrations of $V_{O}^{+2}$ and $O_{i}^{-2}$ are balanced such that $C(V_{O}^{+2}) = C(O_{i}^{-2})$. The charge neutrality point, $\epsilon_{CN}^F$, was found to be 3.0 eV, corresponding to the Fermi energy at which the two lines for $V_{O}^{+2}$ and $O_{i}^{-2}$ intersect in Fig. 2.

The situation is dramatically changed when hafnium is substituted by tantalum; the counter charge of $O_{i}^{-2}$ is now Ta$_{Hf}^{-1}$ instead of $V_{O}^{+2}$ because Ta$_{Hf}^{-1}$ predominates in the vicinity of $\epsilon_{CN}^F$ (Fig. 2). Thus, the charge neutrality condition is satisfied when the concentration of Ta$_{Hf}^{-1}$ is double that of $O_{i}^{-2}$ such that $2C(Ta_{Hf}^{-1}) = C(O_{i}^{-2})$. The charge neutrality point in this case, $\epsilon_{CN}^F$, was found to be 4.1 eV which virtually corresponds to the intersection point of the two lines for $O_{i}^{-2}$ and Ta$_{Hf}^{-1}$. Importantly, $\epsilon_{CN}^F$ is higher than $\epsilon_{CN}^F$ by

![FIG. 2. (Color online) Concentration of positively charged substitutional tantalum for hafnium (Ta$_{Hf}^{+1}$) as a function of Fermi energy in comparison to the concentrations of oxygen vacancies (V$_{O}^{+2}$) and interstitial oxygen (O$_{i}^{-2}$). The lower and upper limits of the Fermi energy correspond to the valence band maximum and conduction band minimum, respectively. The band gap (5.7 eV) was taken from experiment. $\epsilon_{CN}^F$ and $\epsilon_{CN}^N$ indicate the charge neutrality points with and without Ta doping, respectively.](image-url)
1.1 eV. This upward shift of the charge neutrality point on doping with tantalum increases the concentration of \( \text{O}^{1-} \) and decreases the concentration of \( \text{V}^{2+} \), raising the oxygen content of \( \text{HfO}_2 \) (Fig. 2). In other words, doping \( \text{HfO}_2 \) with tantalum increases the oxygen capacity of the material, allowing oxygen to be absorbed from outside. Consequently, the thickness of the \( \text{SiO}_x \) interfacial layer formed between \( \text{HfO}_2 \) and silicon is expected to be reduced when tantalum oxide is deposited on \( \text{HfO}_2 \) (see Fig. 1(b)).

This result conveys the important message that the valency of the cation in an oxide plays a significant role in controlling the oxygen concentration. In a pentavalent oxide such as \( \text{HfO}_2 \), the pentavalent tantalum cation acts as a donor when substituted for hafnium, shifting the charge neutrality point upwards, which results in the increase of the oxygen concentration. In contrast, a trivalent cation would act as an acceptor-type impurity in \( \text{HfO}_2 \), decreasing the concentration of oxygen as a result of the downward shift of the charge neutrality point.

In order to carry this scenario further, we have explored the effects of substituting hafnium in \( \text{HfO}_2 \) by various types of aliovalent impurities. Figs. 3(a) and 3(b) show the change in the oxygen concentration computed by the difference

\[
\Delta C_{\text{O}} = C(\text{O}^{1-}) - C(\text{V}^{2+}), \tag{3}
\]

at the charge neutrality point in each case as a percentage value with respect to the oxygen content in a perfect \( \text{HfO}_2 \) crystal. It is clear that the oxygen concentration is increased on doping with pentavalent cations (V, Nb, and Ta) and decreased on doping with trivalent cations (Sc, Y, and La). Tantalum and scandium doping give the highest and lowest oxygen concentrations, respectively. This is related to the position of their charge neutrality points, i.e., Ta doping gives a highest \( \Delta C_{\text{F}} \), while Sc doping gives the lowest \( \Delta C_{\text{F}} \) for the charge balance \( 2C(\text{Sc}^{1-}) = C(\text{V}^{2+}) \) (Fig. S4). This is attributed to the similarity of their ionic radii with that of hafnium, which allows Ta and Sc to be readily accommodated on the cation site and therefore become good dopants. In contrast, \( \Delta C_{\text{O}} \) is negligible in the cases of vanadium and lanthanum doping because they have very different ionic radii to that of hafnium, are thus difficult to accommodate on the hafnium site, and are unable to shift the charge neutrality point sufficiently (Fig. S4). Therefore, both the valency and ionic radius of the impurity cation are important factors in modifying the oxygen concentration in an oxide.

The advantage of our technique lies in the fact that the interfacial properties can be modified by post-deposition processing. Nano-scale devices require heterostructures that are precisely controlled, yet the quality of an interface is limited by factors involved in the deposition technique, such as the ability to control the vapor pressure of atomic sources. Our method provides a practical solution to this problem: there is no need for precise control of the deposition conditions because one can improve the interfacial structure afterwards, simply by introducing a capping layer. This type of impurity-driven oxygen-flow engineering offers a strategy for the quality control of thin-film stacks in a wide range of materials applications and will open up a field of research in the area of interface physics.

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5See supplementary material at http://dx.doi.org/10.1063/1.3689968 for the chemical potential, density of states, partial charge density, formation energy, and the concentration of dopants in \( \text{HfO}_2 \).