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Theoretical model for artificial structure modulation of $\text{HfO}_2/\text{SiO}_x/\text{Si}$ interface by deposition of a dopant material

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Realization of an abrupt HfO_2/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 HfO_2 layer turns it into an oxygen absorber, suppressing the formation of SiO_x at the interface. Tantalum is predicted as an effective dopant in HfO_2 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 SiO_2/Si interface has facilitated the rapid development of FET-based electrical devices. However, the recent requirement of replacing SiO_2 with a high permittivity (high- κ) oxide such as HfO_2 (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 SiO_x 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 HfO_2 . Substituting a pentavalent tantalum cation for a tetravalent hafnium cation (Ta_{Hf}) donates an extra electron to the lowest available state, namely the conduction band minimum.⁵ The band gap of HfO_2 (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 Ta_{Hf} dopant cations. Rather surprisingly, this electron

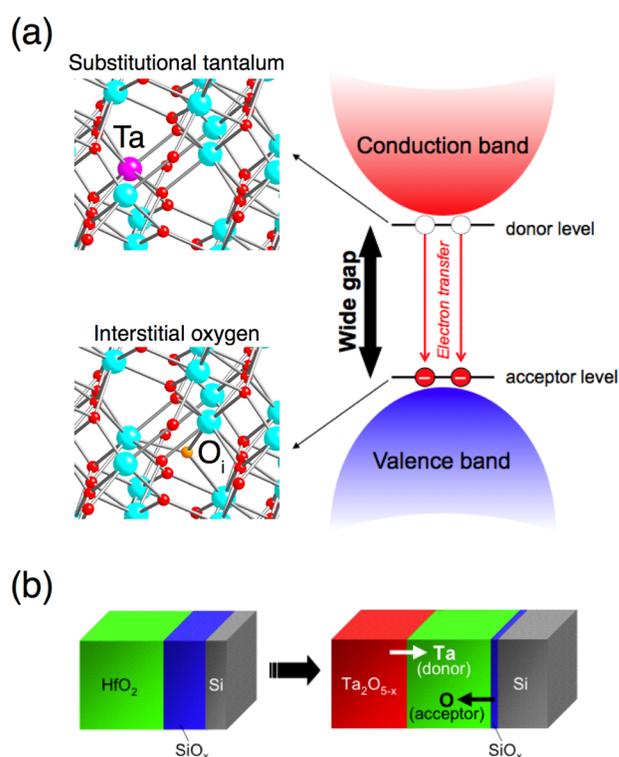


FIG. 1. (Color online) Schematic illustrations of the effect of donor-type impurities in a wide-gap oxide. (a) Electrons occupying high-lying donor levels are in an energetically unstable situation. Therefore, acceptor-type defects are spontaneously formed to accommodate these electrons just above the 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 HfO_2 : substitutional tantalum for hafnium (Ta_{Hf}) 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 HfO_2 are increased on doping with tantalum. (b) Atomic diffusion is driven by capping $\text{HfO}_2/\text{SiO}_x/\text{Si}$ with a layer of $\text{Ta}_2\text{O}_{5-x}$. The capping layer encourages the diffusion of tantalum into HfO_2 , forming Ta_{Hf} , which leads to scavenging of oxygen atoms from SiO_x and hence the formation of O_i . This atomic diffusion reduces the thickness of the SiO_x layer.

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counting concept is indeed valid in ionic compounds such as HfO_2 .⁹ Consequently, the substitution of tantalum for hafnium in HfO_2 promotes the formation of O_i .

This finding offers a practical solution to the undesired formation of SiO_x at the HfO_2/Si interface. According to our theory, HfO_2 becomes an oxygen absorber when doped with tantalum. Therefore, the deposition of a tantalum oxide layer on top of $\text{HfO}_2/\text{SiO}_x/\text{Si}$ may activate the diffusion of oxygen from SiO_x to HfO_2 , restoring an abrupt HfO_2/Si interface (see Fig. 1(b)). In this hypothesis, we assume that oxygen atoms migrate as charge-neutral species because neutral vacancies are relatively stable in SiO_2 due to its covalent nature.¹⁰ The tantalum oxide layer must be slightly oxygen deficient (thus denoted as $\text{Ta}_2\text{O}_{(5-x)}$ in the following) to ensure that oxygen diffuses from SiO_x to HfO_2 rather than from $\text{Ta}_2\text{O}_{(5-x)}$ to HfO_2 .

Our approach is very different from past attempts to reduce the SiO_x layer, which have been based on either capping the $\text{HfO}_2/\text{SiO}_x/\text{Si}$ stack with an oxygen absorber such as metallic titanium¹¹ or AlN ,¹² or on capping with an oxygen barrier such as Al_2O_3 .¹³ These studies represent attempts to control the diffusion of oxygen through the entire $\text{HfO}_2/\text{SiO}_x$ heterostructure. In contrast, our strategy is based on the concept of activating HfO_2 itself to become an oxygen absorber by doping with tantalum.

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.^{14,15} The valence configurations of the pseudo-potentials were $5p^65d^36s^2$ for tantalum, $5p^65d^26s^2$ for hafnium, and $2s^22p^4$ for oxygen. The energy cut-off for the plane-wave basis set expansion was set to 500 eV. A Monkhorst-Pack k-point set of $6 \times 6 \times 6$ was used for a 12-atom unit cell of monoclinic HfO_2 . The optimized lattice constants were $a = 5.04 \text{ \AA}$, $b = 5.11 \text{ \AA}$, $c = 5.21 \text{ \AA}$, and $\beta = 99.74^\circ$, which are in good agreement with the experimental values ($a^{\text{expt.}} = 5.117 \text{ \AA}$, $b^{\text{expt.}} = 5.175 \text{ \AA}$, $c^{\text{expt.}} = 5.291 \text{ \AA}$, 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 ($Q = 0$ 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.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

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

where $E_{\text{tot}}(\text{Ta}_{\text{Hf}}^Q)$ and $E_{\text{tot}}(\text{bulk})$ 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 quanti-

ties μ_{Ta} and μ_{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,⁵ and ϵ_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}^Q is then calculated from the formula

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

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 ϵ_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 $C(V_{\text{O}}^{+2}) = C(\text{O}_i^{-2})$. The charge neutrality point, ϵ_F^{CN} , 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 $\text{Ta}_{\text{Hf}}^{+1}$ instead of V_{O}^{+2} because $\text{Ta}_{\text{Hf}}^{+1}$ predominates in the vicinity of ϵ_F^{CN} (Fig. 2). Thus, the charge neutrality condition is satisfied when the concentration of $\text{Ta}_{\text{Hf}}^{+1}$ is double that of O_i^{-2} such that $2C(\text{Ta}_{\text{Hf}}^{+1}) = C(\text{O}_i^{-2})$. The charge neutrality point in this case, $\epsilon_F^{\text{CN}'}$, was found to be 4.1 eV which virtually corresponds to the intersection point of the two lines for O_i^{-2} and $\text{Ta}_{\text{Hf}}^{+1}$. Importantly, $\epsilon_F^{\text{CN}'}$ is higher than ϵ_F^{CN} by

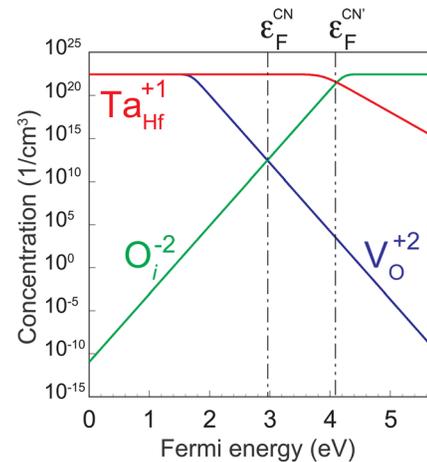


FIG. 2. (Color online) Concentration of positively charged substitutional tantalum for hafnium ($\text{Ta}_{\text{Hf}}^{+1}$) as a function of Fermi energy in comparison to the concentrations of oxygen vacancies (V_{O}^{+2}) and interstitial oxygen (O_i^{-2}). The lower and upper limits of the Fermi energy correspond to the valence band maximum and conduction band minimum, respectively. The band gap (5.7 eV) was taken from experiment.⁶ $\epsilon_F^{\text{CN}'}$ and ϵ_F^{CN} indicate the charge neutrality points with and without Ta doping, respectively.

1.1 eV. This upward shift of the charge neutrality point on doping with tantalum increases the concentration of O_i^{-2} and decreases the concentration of V_O^{+2} , raising the oxygen content of HfO_2 (Fig. 2). In other words, doping HfO_2 with tantalum increases the oxygen capacity of the material, allowing oxygen to be absorbed from outside. Consequently, the thickness of the SiO_x interfacial layer formed between HfO_2 and silicon is expected to be reduced when tantalum oxide is deposited on 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 tetravalent oxide such as 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 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 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

$$\Delta C_O = C(O_i^{-2}) - C(V_O^{+2}), \quad (3)$$

at the charge neutrality point in each case as a percentage value with respect to the oxygen content in a perfect 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).

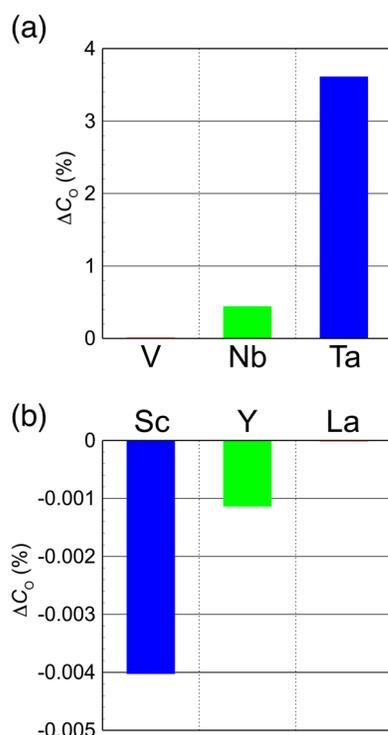


FIG. 3. (Color online) Change in oxygen concentration (ΔC_O) on doping with aliovalent impurities with respect to a perfect HfO_2 crystal for (a) donors and (b) acceptors.

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 ϵ_F^{CN} , while Sc doping gives the lowest ϵ_F^{CN} for the charge balance $2C(Sc_{Hf}^{-1}) = C(V_O^{+2})$ (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, ΔC_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 HfO_2 .

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