

## Comparative study of defect energetics in HfO<sub>2</sub> and SiO<sub>2</sub>

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We perform *ab initio* calculations, based on density functional theory, for substitutional and vacancy defects in the monoclinic hafnium oxide (*m*-HfO<sub>2</sub>) and  $\alpha$ -quartz (SiO<sub>2</sub>). The neutral oxygen vacancies and substitutional Si and Hf defects in HfO<sub>2</sub> and SiO<sub>2</sub>, respectively, are investigated. Our calculations show that, for a large range of Hf chemical potential, Si substitutional defects are most likely to form in HfO<sub>2</sub>, leading to the formation of a silicate layer at the HfO<sub>2</sub>/Si interface. We also find that it is energetically more favorable to form oxygen vacancies in SiO<sub>2</sub> than in HfO<sub>2</sub>, which implies that oxygen-deficient HfO<sub>2</sub> grown on top of SiO<sub>2</sub> will consume oxygen from the SiO<sub>2</sub>. © 2004 American Institute of Physics. [DOI: 10.1063/1.1650874]

The continuous device miniaturization in the microelectronic industry will eventually lead, within the present technology, to the end of the use of amorphous SiO<sub>2</sub> (*a*-SiO<sub>2</sub>) as gate dielectric in metal-oxide-semiconductor field-effect transistors. The existence of a thickness limit for the *a*-SiO<sub>2</sub> around 10–12 Å, has clearly been established experimentally.<sup>1</sup> One way to circumvent this problem, still keeping Si as the basic device material, is to employ high-permittivity materials as alternative gate dielectrics in place of the conventional *a*-SiO<sub>2</sub>. Among them, hafnium oxide is emerging as the material with greatest potential to substitute SiO<sub>2</sub>, due mainly to its high dielectric constant and thermodynamic stability when it forms an interface with Si.

Even though hafnium oxide is thermodynamically stable against an overall decomposition as Hf and SiO<sub>2</sub> when grown on Si, interfacial reactions can occur. Thereby, the formation of a thin interfacial layer (oxides, silicates and silicides) between the HfO<sub>2</sub> and the Si surface, has been recently observed.<sup>2,3</sup> This interfacial layer occurs during almost any film growth processes or post-annealing, which is an intrinsic part of any growth cycle. Therefore, the thermodynamic stability of the hafnium oxide in contact with silicon is identified as a critical issue for the application of alternative gate dielectric in silicon-based devices.<sup>4,5</sup> Moreover, the study of possible defects related to the migration of atoms across the interface is of fundamental importance. In particular, a significant source of defects in this system is the interface itself, which has been shown<sup>6</sup> to consist of Hf silicates with a dielectric constant lower than that of HfO<sub>2</sub>.<sup>7,8</sup>

In the present work, we address the formation of neutral defects through first-principles calculations, based on density functional theory (DFT). We analyze the formation of Si substitutional defects in HfO<sub>2</sub>, as well as Hf substitutional defects in SiO<sub>2</sub>, for different growth conditions. Finally, the energetics of an oxygen vacancy in SiO<sub>2</sub> is compared to a similar vacancy in HfO<sub>2</sub>, in order to understand the growth of hafnium oxide under oxygen-poor conditions.

Many experimental works<sup>9–12</sup> have addressed the chemical reactions that could occur in the HfO<sub>2</sub>/Si interface during

the HfO<sub>2</sub> growth cycle. This is due in order to prevent and/or control the interfacial layer formation. Almost all work has reported the formation of an interfacial Hf silicate in oxygen-rich atmospheres. Furthermore, Wang and co-workers<sup>13</sup> have shown that under opposite conditions (i.e., oxygen-deficient atmospheres), the Hf silicate interfacial formation does not happen during the HfO<sub>2</sub> growth cycle. However, there are still many open questions, such as which atomic species are migrating when the interfacial silicate is formed. For example, it is important to know if Hf will be incorporated in a formed SiO<sub>2</sub> layer, or if Si from either the bulk Si or this SiO<sub>2</sub> layer will be incorporated in the HfO<sub>2</sub>.

The DFT calculations were performed using ultrasoft Vanderbilt pseudopotentials,<sup>14</sup> and the generalized gradient approximation for the exchange-correlation potential as implemented in the VASP code.<sup>15–18</sup> In order to study the defects in the different systems we have considered the monoclinic HfO<sub>2</sub> and the  $\alpha$ -quartz (SiO<sub>2</sub>) crystalline phases, using a 96 and 72 atom supercells, respectively. For these cells, we have used a plane wave cutoff energy of 400 eV and a 2×2×2 Monkhorst–Pack **k**-mesh. These crystal structures have been previously used to describe these systems.<sup>19–21</sup> In all calculations, the atoms were allowed to relax until all components of the atomic forces were smaller than 0.025 eV/Å.

The silicon substitutional defect (Si<sub>Hf</sub>) was created in the *m*-HfO<sub>2</sub> supercell by substitution of one hafnium atom by one silicon atom in the equilibrium perfect crystal. On the other hand, the hafnium substitutional defect (Hf<sub>Si</sub>) was created in the  $\alpha$ -quartz by substitution of one silicon atom by one hafnium atom in the equilibrium perfect crystal. Our results show that the presence of either Si<sub>Hf</sub> or Hf<sub>Si</sub> in HfO<sub>2</sub> or SiO<sub>2</sub>, respectively, do not introduce any additional active levels in the bandgap. For the perfect HfO<sub>2</sub> at the equilibrium, we obtain an indirect bandgap of 3.9 eV along  $\Gamma$ –B. For this same supercell, the density of states shows that the O 2*s* and O 2*p* bands are centered at around –17.2 and –2.8 eV, with bandwidth of approximately 2.1 and 5.6 eV, respectively, whereas the Hf 5*d* band is centered at around 5 eV forming the conduction band, with bandwidth of 2.6 eV. These results are in good agreement with previous DFT calculations of this material.<sup>22</sup> Moreover, for HfO<sub>2</sub> with a Si

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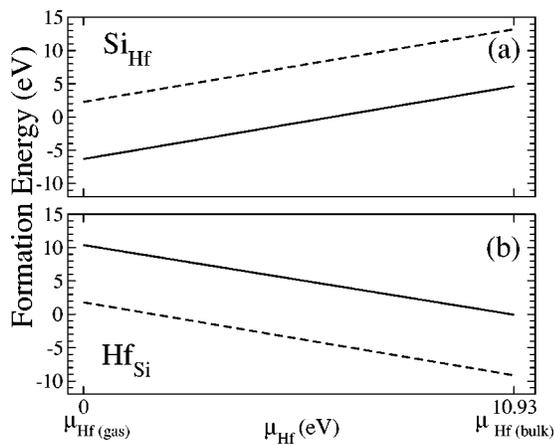


FIG. 1. Formation energies for the two substitutional defects considered in this work: (a) Si in place of a Hf in  $\text{HfO}_2$  and (b) Hf in place of a Si in  $\text{SiO}_2$ . The formation energies are plotted as a function of the Hf chemical potential, and for two values of the Si chemical potential, the bulk Si chemical potential (solid curves) and the chemical potential for Si in the  $\text{SiO}_2$  under an oxygen-rich environment (dashed curves).

substitutional defect, we observe a resonant state around 6.9 eV below the top of the valence band, which is related to the  $\text{O } 2p$ -like and Si bonding state.<sup>23</sup>

The formation energy for a  $\text{Si}_{\text{Hf}}$  is expressed as

$$E_f^{\text{Si}_{\text{Hf}}} = [E_t(\text{Si}_{\text{Hf}}) + \mu_{\text{Hf}}] - [E_t(\text{HfO}_2) + \mu_{\text{Si}}], \quad (1)$$

whereas for  $\text{Hf}_{\text{Si}}$  the analogous expression is

$$E_f^{\text{Hf}_{\text{Si}}} = [E_t(\text{Hf}_{\text{Si}}) + \mu_{\text{Si}}] - [E_t(\text{SiO}_2) + \mu_{\text{Hf}}]. \quad (2)$$

In these expressions,  $E_t(D_S)$  are the total energies of the fully relaxed supercells (either  $m$ - $\text{HfO}_2$  or  $\text{SiO}_2$ ) with the substitutional defect  $D_S$ , and  $E_t(\text{XO}_2)$  are the total energies of the similar supercells for the perfect crystals of  $\text{XO}_2$  ( $X = \text{Hf}$  or  $\text{Si}$ ). The values of the chemical potentials  $\mu_{\text{Hf}}$  and  $\mu_{\text{Si}}$  depend on the growth conditions. We have considered two limits for  $\mu_{\text{Hf}}$ . (i) The bulk metal as a reference, which would correspond to a Hf-rich growth condition and the formation of Hf clusters in the bulk or at the surface of the oxide. (ii) Under oxygen-rich conditions, considering that there are plenty of oxygen atoms in the  $\text{HfO}_2$ ,<sup>24</sup> such that the removed hafnium remains always in equilibrium with the gaseous oxygen the  $\mu_{\text{Hf}}(\text{gas})$  can be obtained as  $\mu_{\text{Hf}}(\text{gas}) = \mu_{\text{HfO}_2} - \mu_{\text{O}_2}$ . The  $\text{HfO}_2$  chemical potential ( $\mu_{\text{HfO}_2}$ ) was obtained as the energy per unit formula for the monoclinic bulk hafnium oxide, and  $\mu_{\text{O}_2}$  is the energy of an isolated oxygen molecule, which was obtained through a DFT total energy calculation for an  $\text{O}_2$  inside a cubic supercell of 15 Å side. For the silicon chemical potential, two similar limits were considered: (i)  $\mu_{\text{Si}}$  as the crystalline bulk Si chemical potential, and (ii)  $\mu_{\text{Si}}$  as the chemical potential of Si in  $\text{SiO}_2$  under oxygen rich conditions; that is,  $\mu_{\text{Si}} = \mu_{\text{SiO}_2} - \mu_{\text{O}_2}$ , with  $\mu_{\text{O}_2}$  as discussed earlier and  $\mu_{\text{SiO}_2}$  obtained as the energy per unit formula of  $\alpha$ -quartz.

The results for the formation energies are presented in Fig. 1. As can be seen from Fig. 1(a), under oxygen-rich conditions, the formation of a Si substitutional defect in  $\text{HfO}_2$  is very likely to occur, especially if the Si source is the bulk crystal. Under this O-rich situation, the formation of this defect would only become unfavorable if a thick enough

layer of  $\text{SiO}_2$  exists between the Si substrate and the  $\text{HfO}_2$ . In this case, either the source of Si atoms would be the silica, or the Si would somehow not diffuse through this thick layer. If the  $\text{SiO}_2$  is thin enough, such that the Si diffusion through it is significant, then the formation of a Hf silicate (at least close to the interface) seems unavoidable.<sup>25</sup> On the other hand, under Hf-rich conditions, it is less likely that Si substitutional defects in  $\text{HfO}_2$  will be formed.

The formation of Hf substitutional defects in  $\text{SiO}_2$  has a behavior that is opposite to  $\text{Si}_{\text{Hf}}$ , as can be seen in Fig. 1(b); that is, it is not likely to form under oxygen-rich conditions, and becomes more probable under Hf-rich conditions. In a situation in which the Si chemical potential is given by its bulk value (either thin or no  $\text{SiO}_2$  layer), the formation of a  $\text{Hf}_{\text{Si}}$  in  $\text{SiO}_2$  is unlikely to happen, for a large range of Hf chemical potential. These results show the importance of performing reliable *ab initio* calculations. One could, in principle, consider it obvious that under Hf-rich conditions a Hf substitutional defect would be formed in  $\text{SiO}_2$ . However, as shown earlier, this depends on the Si chemical potential.

We also considered the formation of neutral oxygen vacancies ( $V_{\text{O}}$ ), both in  $\text{SiO}_2$  as well as in  $\text{HfO}_2$ ,<sup>21</sup> since they can be created in films and bulk samples due to the growth cycle. The neutral oxygen vacancy in the  $m$ - $\text{HfO}_2$  and  $\alpha$ -quartz were generated by simple removal of an oxygen atom, followed by full relaxation of all remaining atoms. The formation energies for a  $V_{\text{O}}$  in  $\text{XO}_2$  ( $X = \text{Hf}$  or  $\text{Si}$ ),  $E_f(V_{\text{O}})$ , were calculated as

$$E_f^{\text{XO}_2}(V_{\text{O}}) = [E_t^{\text{XO}_2}(V_{\text{O}}) + \mu_{\text{O}}] - [E_t(\text{XO}_2)], \quad (3)$$

where  $E_t^{\text{XO}_2}(V_{\text{O}})$  and  $E_t(\text{XO}_2)$ , are the total energies of supercells of  $\text{XO}_2$  ( $X = \text{Hf}$  or  $\text{Si}$ ) with and without an oxygen vacancy, respectively. The oxygen chemical potential  $\mu_{\text{O}}$  was considered either as the total energy of an isolated oxygen atom, or as one half of the energy of an isolated oxygen molecule (in both cases, the  $\text{O}_2$  triplet ground state was used). The monoclinic phase has nonequivalent oxygen atoms (i.e., in which some sites are threefold coordinated), whereas others are fourfold coordinated by hafnium atoms. In this way, we have determined the formation energy for both vacancy types using Eq. (3), and we obtain a formation energy difference around 0.02 eV. In the former case, we obtained of  $E_f^{\text{HfO}_2}(V_{\text{O}}) = 9.32$  eV and  $E_f^{\text{SiO}_2}(V_{\text{O}}) = 8.10$  eV, whereas for the latter choice of  $\mu_{\text{O}}$ , we obtained  $E_f^{\text{HfO}_2}(V_{\text{O}}) = 6.38$  eV and  $E_f^{\text{SiO}_2}(V_{\text{O}}) = 5.16$  eV. This indicates that, although neutral oxygen vacancies are energetically unfavorable in both materials, they are more stable in silicon oxide than in hafnium oxide, by approximately 1.23 eV. This implies that, if an oxygen-deficient  $\text{HfO}_2$  is grown on top of a  $\text{SiO}_2$  layer, oxygen atoms will migrate from  $\text{SiO}_2$ . In this way, oxygen vacancies are created in the silica layer toward the  $\text{HfO}_2$ , healing at the sometimes oxygen vacancies in the hafnia. Indications that this process does indeed occur, has been recently reported.<sup>13</sup>

In summary, our results show that, unless the hafnium chemical potential is always very close to its bulk value (i.e., oxygen-poor growth conditions), the formation of Si substitutional defects in the  $\text{HfO}_2$  is almost unavoidable. This will lead to the formation of a silicate-like layer close to the in-

terface. For a very large range of Hf chemical potential it is very likely that incoming silicon atoms from the Si substrate will form a  $(\text{HfO}_2)_x(\text{SiO}_2)_y$  layer, as supported by experimental observations.<sup>25</sup> The only way to prevent the formation of a silicate layer would be through the use of an oxygen-deficient  $\text{HfO}_2$ , as has been observed.<sup>13</sup> However, even if this silicate formation is prevented in the initial steps of dielectric growth, it seems almost impossible that it will not be formed given the necessary further thermal processing steps, unless a barrier for the Si diffusion being introduced.<sup>9</sup>

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