A study of Hf vacancies at Si:HfO$_2$ heterojunctions

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In this work we have investigated the formation and migration of Hf vacancies in a Si:HfO$_2$ heterostructure based on first principles calculations. Our calculations indicate that Hf vacancies tend to diffuse from bulk HfO$_2$ to the Si:HfO$_2$ interface and that it is energetically favorable for Si atoms to fill the interfacial Hf vacancies. These results provide a plausible mechanism of the formation of interfacial Hf silicates. © *2008 American Institute of Physics.*
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In an attempt to find a suitable replacement for conventional SiO$_2$ gate dielectrics in microelectronic devices to enable continued miniaturization, high dielectric constant materials such as HfO$_2$ have been extensively studied in recent years.[1–3] Although HfO$_2$ is expected to be thermodynamically stable in contact with Si substrates, undesirable interfacial phases such as silicides, silicates, and silica have been reported,[4–9] depending on the processing atmospheres. Understanding the mechanisms underlying the formation of such unexpected interfacial phases is essential to suppress their formation and to enhance device performances. It has been proposed that these interfacial reactions could be closely related to high diffusivity of oxygen and due to deviations from the ideal stoichiometry of the deposited HfO$_2$.[10] Indeed, our previous calculations have indicated that the diffusion and segregation of O vacancies and interstitials to the Si:HfO$_2$ interface could contribute to the formation of interfacial Hf silicides[11] and SiO$_x$,[12] respectively.

Although less common than O defects, Hf vacancies could also account for the deviation from ideal stoichiometry of HfO$_2$. In this work, through a set of density functional theory (DFT) based computations, we show that the presence of Hf vacancies could lead to the formation of hafnium silicate type interfacial phases.

DFT calculations were performed using the VASP code[13] with the Vanderbilt ultrasoft pseudopotentials,[14] the generalized gradient approximation utilizing the PW91 functional,[15] and a cutoff energy of 400 eV for the plane wave expansion of the wavefunctions. Monkhorst–Pack k-point meshes of $2 \times 2 \times 1$ and $2 \times 2 \times 2$ were used for the Si:HfO$_2$ interface models and bulk HfO$_2$, respectively.

Our epitaxial Si:HfO$_2$ heterostructures (Fig. 1, left) were constructed by placing a (001) monoclinic hafnia (m-HfO$_2$) slab on a (001) Si slab such that their [100] directions coincide with each other.[12] The equilibrium lattice constants a, b, and c of m-HfO$_2$ were determined to be 5.14, 5.19, and 5.30 Å, respectively, in good agreement with the corresponding experimental values of 5.12, 5.17, and 5.29 Å,[16] and the lattice constant of Si was calculated to be 5.46 Å, also in good agreement with the experimental value of 5.43 Å.[17] In our Si:HfO$_2$ epitaxial models, the lattice constants a and b of the m-HfO$_2$ building blocks were stretched to match Si lattice constant (and c was optimized), resulting in strains of

6% and 5% in HfO$_2$ along a and b, respectively. The Si:HfO$_2$ heterojunction model contained nine Si and six Hf layers, and each Si layer contained eight atoms (corresponding to a 2×2 cell or 10.92×10.92 Å^2 along the interface plane). The dangling bonds of the top (Hf) and bottom (Si) free surfaces of the heterostructures were passivated by adding half monolayer of O atoms,[12] and a vacuum of about 10 Å separated the whole structure from its image along the interface normal. O-terminated interfaces were considered here, as these have been shown earlier to be more stable and desirable than Hf-terminated ones.[18] After geometry optimization, half of the interface O atoms contributed to the formation of Si–O–Si bonds, while the other half resulted in Hf–O–Hf bonds, as shown in Fig. 1 (left). This configuration allows for the passivation of all interface atoms as prescribed by the bond counting arguments of Peacock *et al.*[18]

Hf vacancy formation energies were calculated for various sites along the Si:HfO$_2$ interface normal to investigate the thermodynamic driving forces for the segregation of the Hf vacancy to the Si:HfO$_2$ interface. The formation energy of a Hf vacancy can be defined as

$$E_f = E_{vac} - E_{perf} + E_{Hf}, \qquad (1)$$

where E_{vac} and E_{perf} represent the energies of the system with a Hf vacancy and the perfect system, respectively, and E_{Hf} is the energy of a Hf atom. In Eq. (1), E_{Hf} can be the energy of a Hf atom either in a bulk Hf crystal or in a bulk m-HfO$_2$ crystal.[19] The specific choice for the E_{Hf} value is not critical as we are interested only in the relative E_f values at various Hf vacancy positions. Here, we use latter definition for E_{Hf}, which was determined as $E_{HfO_2} - E_{O_2} = -20.95$ eV, with E_{HfO_2} and E_{O_2} being the energy per formula unit of m-HfO$_2$ and the energy of an isolated O$_2$ molecule, respectively.

Hf vacancies far from the Si:HfO$_2$ interface were treated using a $2 \times 2 \times 2$ unit cell of the strained bulk m-HfO$_2$, which contained 32 Hf and 64 O sites. The lattice vectors a and b of m-HfO$_2$ were stretched to match the equilibrium Si lattice constant. As HfO$_2$ in the Si:HfO$_2$ heterojunction contained the same level of strain, we believe that the impact of strain on the vacancy formation and migration energies (to be discussed below) could be consistently factored out. Previous calculations on bulk HfO$_2$ indicate that two Hf vacancies can be stabilized by forming Hf vacancy pair.[20] In view of the fact that the deviation from the perfect HfO$_2$ stoichiometry is generally small,[21] we only considered an isolated Hf vacancy during our calculations. E_f was computed to be

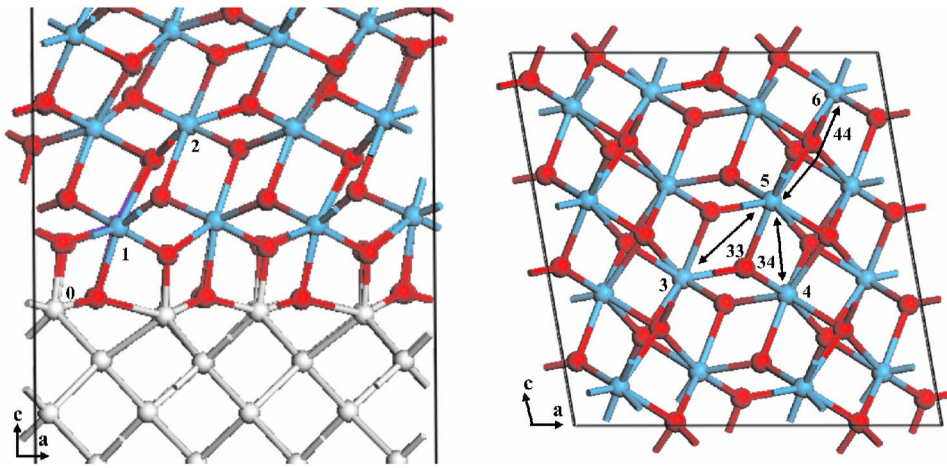**92**, 152911-1

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FIG. 1. (Color online) Si: white, Hf: blue (gray), O: red (dark gray). (Left) Interfacial configuration of Si:HfO$_2$ heterostructure. (Right) Bulk monoclinic HfO$_2$.

3.8 eV, about 2.3 eV lower than its counterpart for the unstrained bulk HfO$_2$. Near the Si:HfO$_2$ interface, Hf vacancy was studied by removing a Hf atom from sites 1 or 2 (Fig. 1, left), and the corresponding E_f were −0.9 and −0.3 eV, respectively. The large decrease in E_f near the interface represents the energetic favorability for Hf vacancies to segregate from bulk HfO$_2$ to the interface. Since in reality bulk HfO$_2$ is less strained than modeled here, while the interface is close to the modeled, the true decrease in E_f as the Hf vacancy moves from bulk HfO$_2$ to the Si:HfO$_2$ interface is expected to be even greater than predicted here. Similar trends have been found for O defects in Si:HfO$_2$ (Refs. 11 and 12) and defects in other oxides.[22]

To explore the kinetic barriers for Hf vacancy segregation to the interface, we performed migration calculations using the nudged elastic band method.[23] For all migration calculations we used the same supercells as those for E_f calculations. In bulk HfO$_2$ two neighboring Hf atoms can be mutually coordinated to different types of O atoms. For example, sites 3 and 5 (Fig. 1, right) share two threefold coordinated O atoms, sites 4 and 5 share one threefold and one fourfold coordinated O atoms, and sites 5 and 6 share two fourfold coordinated O atoms. Correspondingly, we considered three Hf vacancy migration paths labeled as 33, 34, and 44, as indicated by the arrows in Fig. 1 (right). The migration distances, defined as the Hf–Hf distances along the migration paths in a defect-free system, are almost identical along paths 33 and 34 (3.38 Å). Path 44 here considered is about 0.2 Å longer than paths 33 and 34. The barriers along paths 33, 34, and 44 were calculated to be 2.4, 1.5, and 6.0 eV, respectively. Near the Si:HfO$_2$ interface neighboring Hf atoms are connected by threefold coordinated O atoms (i.e., corresponding to path 33 in bulk HfO$_2$), and the distance between sites 1 and 2 is 3.48 Å. The barrier for Hf vacancy migration from sites 2 to 1 was calculated to be 2.1 eV, about 0.3 eV lower than that for path 33 in bulk HfO$_2$. All the barrier values together with the vacancy formation energies are listed in Table I and plotted in Fig. 2 to show a Hf vacancy migration energy profile. All energies in this figure represented as open square symbols correspond to those of the "images" of the nudged elastic band computations (i.e., initial, final, and intermediate geometric configurations during migration). Energies are defined relative to $(E_{perf} - E_{Hf})$, so that the energies of the minima (marked by vacancy site numbers) correspond to vacancy formation energies. The fig-

ure shows an obvious trend that Hf vacancies segregate from bulk HfO$_2$ toward the Si:HfO$_2$ interface.

The presence of Hf vacancies near Si:HfO$_2$ interfaces leaves open the possibility that Si atoms could migrate into the HfO$_2$ side, allowing for the "nucleation" of interfacial Hf silicate phases. To check whether this is feasible, we considered the process of switching the positions of the Hf vacancy at site 1 and the Si atom at site 0 (Fig. 1, left). We found that the energy of the system dropped by 2.4 eV when the Si atom occupied the originally vacant site 1, leaving a Si vacancy at site 0. Creation of Si–O bonds thus appears to be favored at the interface. This is consistent with our previous Si:HfO$_2$ calculations, where the penetration of an O interstitial from HfO$_2$ side into Si side decreased the system energy by more than 2 eV.[12] These Si migration results are also displayed in Fig. 2 with solid squares. The barrier for Si migration to site 1 was calculated to be 0.2 eV. The large thermodynamic driving force and the low migration barrier make the penetration of Si atoms into HfO$_2$ side almost a certainty in the presence of Hf vacancies.

Whether or not Si atoms will penetrate further into HfO$_2$ was also addressed. To understand the thermodynamic factors, we calculated the energy needed to replace a Hf atom by a Si atom near the Si:HfO$_2$ interface and in bulk HfO$_2$. The required energy is defined as

$$E_s = E_{subs} - (E_{perf} + E_{Si} - E_{Hf}), \quad (2)$$

where E_{subs} and E_{perf} represent the energies of the system with a substitutional Si and the perfect system, respectively, and E_{Si} (E_{Hf}) is the energy of a Si (Hf) atom. We found E_s in bulk HfO$_2$ was 0.07 eV higher than that for Hf to be replaced by Si at the first interfacial Hf layer. Thus, from an energetic point of view, Si displays a roughly equal preference to be at

TABLE I. Hf vacancy formation (E_f) and migration (E_m) energies (eV) in Si:HfO$_2$ heterostructure. Refer to Fig. 1 for definition of vacancy site and migration path labels.

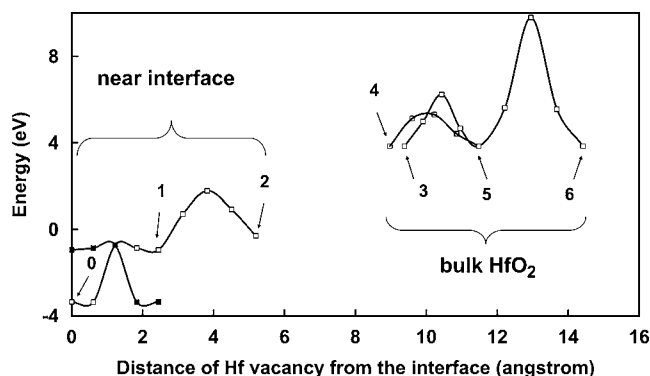|	Vacancy site	E_f	Migration path	E_m
Bulk	⋯	⋯	5–3 (33)	2.4
HfO$_2$	any	3.8	5–4 (34)	1.5
			5–6 (44)	6.0
Near	2	−0.3	2–1	2.1
Interface	1	−0.9	1–0 (Si: 0–1)	0.2
	0 (Si at 1)	−3.3		

FIG. 2. Hf vacancy migration profiles for Si:HfO$_2$ heterostructure. Hf vacancy results are shown in open squares. Solid squares represent the hopping of Si from sites 0 to 1. See Fig. 1 for definition of site indices.

based computations. These results provide a plausible mechanism for the formation of interfacial Hf silicate phases experimentally observed.

the Si:HfO$_2$ interface or in bulk HfO$_2$. Next, we performed calculations on Si migration to its neighboring Hf vacancy sites in bulk HfO$_2$. The same HfO$_2$ supercell shown in Fig. 1 (right) was employed here, but with one Hf atom replaced by Si (and a neighboring Hf site vacant). We considered the paths 33 and 34, for which the migration barriers were calculated to be 2.1 and 7.8 eV, respectively. The migration barrier for Si penetration (through a vacancy mechanism) in bulk HfO$_2$ along the 33 path is thus a little smaller than the same process for a Hf atom. Nevertheless, it must be mentioned that Si penetration into bulk HfO$_2$ should be aided by the presence of Hf vacancies. We thus conclude that in the presence of the right environment (e.g., vacancies, grain boundaries, etc.), Si penetration could be at least as facile as Hf vacancy migration in bulk HfO$_2$. Nevertheless, of all the processes considered in this work, migration of a Si atom across the Si:HfO$_2$ interface in the presence of interfacial Hf vacancies is the most favored and dramatic.

In summary we have illustrated the trend of Hf vacancy diffusion from bulk HfO$_2$ to Si:HfO$_2$ interfaces, and the subsequent penetration of Si across the interface, using DFT

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