Impurity segregation and ordering in $Si/SiO_2/HfO_2$ structures

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We use first-principles calculations and experimental data to demonstrate that impurity segregation at heterointerfaces is governed by several factors. In particular, Hf impurities avoid the $Si\text{-}SiO_2$ interface when present in the SiO_2 side, might segregate if present in the Si side, but do not cross into SiO_2. Substitutional Hf impurities in SiO_2, as revealed by a through-focal series of *Z*-contrast images, act as markers for Si sites, suggesting ordering in the first two Si planes of the amorphous SiO_2. Finally, we show that dopants in Si segregate at the interface by adopting several distinct configurations and also do not cross into SiO_2.

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I. INTRODUCTION

Impurity segregation at interfaces and grain boundaries has long been known to play a major role in determining many properties of complex materials and structures.[1] The generic reason for the seemingly ubiquitous phenomenon is that interfaces provide a more diverse environment that allows different bonding arrangements and more flexible relaxations. The latter is especially true at crystalline-amorphous interfaces, such as the $Si\text{-}SiO_2$ interface. For example, it has long been known that dopant impurities such as As, P, and B segregate at the $Si\text{-}SiO_2$ interface.[2–4] Recently, however, atomically resolved *Z*-contrast imaging of stray Hf atoms inside the SiO_2 interlayer of $Si/SiO_2/HfO_2$ structures found that the Hf atoms *avoid* the $Si\text{-}SiO_2$ interface.[5–7] Such multilayer structures are widely studied as a possible replacement of pure SiO_2 as the gate dielectric in advanced microelectronics, whereby a fundamental understanding of the behavior of stray impurities and other defects has become important.[5,8,9]

Impurity segregation in grain boundaries occurs because configurations at the boundary have a lower free energy than those in the bulk.[1] In *A*-*B* heterointerfaces, segregation is a much more complicated issue and so far has not been examined in detail. In principle, an impurity may segregate if it is present in either material. Alternatively, it may segregate if it is present in material *A*, but it avoids the interface if it is present in material *B*. In addition, the interface may or may not act as a barrier against the diffusion of an impurity to the other side.

In this paper, we report a systematic study that demonstrates these possibilities for Hf and dopant impurities and the $Si\text{-}SiO_2$ interface. The computational framework employed is outlined in Sec. II. In that section, the structural models that we used are also described. In Sec. III, by using energies from density-functional calculations complemented with formation entropies, we first establish that Hf impurities in SiO_2 prefer to substitute for Si atoms; interstitial Hf causes significant rebonding with much higher formation energies. We further show that the free energy of substitutional Hf rises near the interface and two Hf atoms avoid sharing a bridging O atom. Thus, we account for the experimental observation that *Hf atoms originating in the oxide stay dispersed and avoid the interface*.[5–7] We also report calculations that probe the segregation of Hf if diffused in from the Si side. The results show that Hf atoms in bulk Si can lower their energy by pairing, which suggests the possibility of clustering. Nevertheless, isolated Hf atoms reaching the interface would segregate at the interfacial plane and form two Hf-O bonds but would not enter the oxide.

We further infer that, being substitutional, the observed Hf atoms act as markers for Si sites in the oxide. This has allowed us to study the ordering of Si planes within the vicinity of the $Si\text{-}SiO_2$ interface (Sec. IV) by taking full advantage of *Z*-contrast imaging. More specifically, we performed an extensive analysis of the *Z*-contrast images obtained by using an aberration-corrected scanning transmission electron microscope.[5] A through-focal series of the images provides a reconstruction of the positions of all Hf atoms within the SiO_2 interlayer (see Fig. 1, in which Hf atoms appear as encircled bright spots). A histogram was constructed from the observed Hf sites. A comparison to histograms of Si sites in model $Si\text{-}SiO_2$ structures reveals ordering of Si planes in the interfacial region of the amorphous

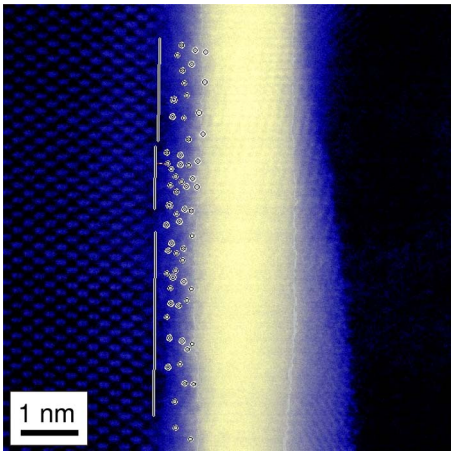

FIG. 1. (Color online) *Z*-contrast STEM image of the $Si/SiO_2/HfO_2$ structure. Stray Hf atoms inside the SiO_2 interlayer are encircled. The vertical lines represent the location of the $Si\text{-}SiO_2$ interface plane.

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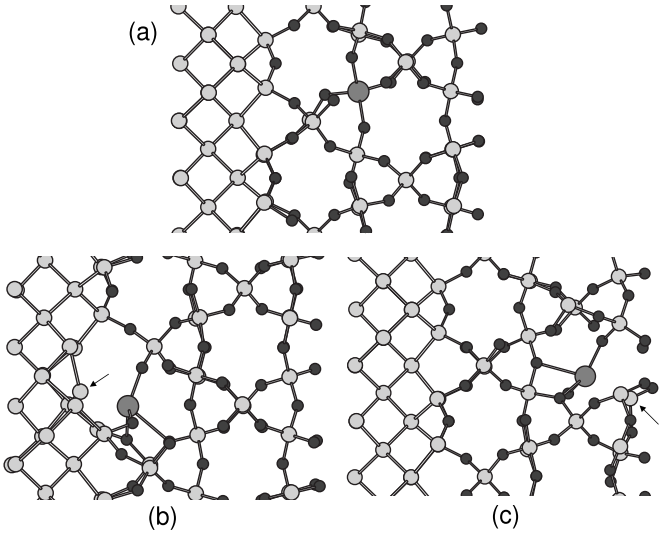

FIG. 2. Minimum energy configurations for Hf atoms (large gray spheres) in SiO_2 close to the Si-SiO_2 interface: (a) substitutional and [(b) and (c)] interstitial defects. Si (O) atoms are depicted as larger (smaller and dark) spheres. The arrows mark undercoordinated Si atoms. Only parts of the actual unit cells are displayed [here and in Figs. 3–6].

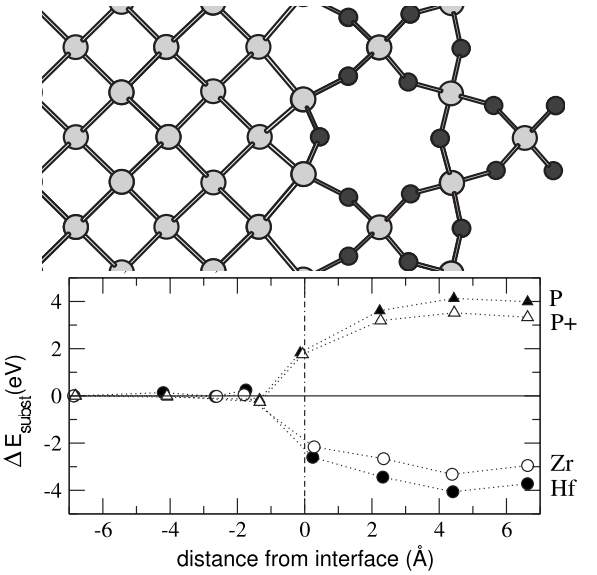

FIG. 3. Formation energies of substitutional impurities and dopants in Si-SiO_2.

SiO_2 layer. Next, in Sec. V, we present our analysis of the segregation of dopant impurities (P and As) to the Si-SiO_2 interface. Isolated dopant impurities in Si behave similarly to Hf. However, the source of the energy gain from segregation is different. *Dopants avoid forming bonds with O atoms across the interface*; instead, they segregate either as single impurities or as pairs in the subinterface region, gaining energy from relaxations of the nearby oxide network and/or by achieving a threefold coordination. Finally, our concluding remarks are presented in Sec. VI.

II. COMPUTATIONAL FRAMEWORK

The calculations were based on density-functional theory and the projector-augmented wave method[10] as implemented in the VASP code.[11] The generalized-gradient approximation was used for exchange correlation, an approximation that provides the correct ground-state energetics for SiO_2.[12] Our Si-SiO_2 supercell had perfect stoichiometry and a three-dimensional periodicity and was constructed according to the procedure devised in Ref. 13. The cell comprised 11 planes of crystalline Si and a SiO_2 slab up to 1.8 nm thick, with in-plane cell dimensions of 7.73×12.22 Å^2 and a total of 141 atoms, allowing minimal interactions of the impurities with their images in the neighboring cells. A quartzlike structure was chosen for SiO_2 with its *c* axis aligned parallel to the [001] cube axis of the Si substrate, leading to an epitaxial fit with the Si (100) surface with no coordination defects. The resulting stoichiometric abrupt interface [see Figs. 2(a) and 3] was found to have the lowest energy by previous *ab initio* calculations,[13] a result that was traced to two factors: the tendency of the Si (001) surface to impose order at the nominal interface plane and the ability of the Si-O-Si bridges to pivot about the O atom (as opposed to the very strong resistance against bending of the stiff, covalent Si-Si bond). Although Si-Si suboxide bonds (O vacancies) near the interface are energetically costly, it was also shown[13] that they can be favored by entropic considerations or form at domain boundaries of the Si-SiO_2 interface. The purpose of the present paper is to study the energetically preferred sites for Hf and other impurities in the vicinity of an abrupt Si-SiO_2 interface. Reactions of Hf atoms with other defects near the interface, such as suboxide bonds or oxygen protrusions, is beyond the scope of the present study (an interfacial suboxide bond in which one of the Si atoms is replaced by Hf was the subject of a recently published paper[14]).

For selected cases involving the incorporation of Hf impurities at and near the Si-SiO_2 interface, a tridymitelike polymorph was also employed for comparison. The HfO_2 layer that was present in the experimental samples is not included in our model structure since we were mainly interested in the near-interface region of Si-SiO_2. Therefore, an implicit assumption is made that since the HfO_2 layer is relatively far (at least 8 Å away from the nominal interface plane), it does not play a major role in determining the energetically preferred configurations of Hf atoms within the vicinity of the Si-SiO_2 interface. This assumption turned out to be justified as we shall discuss in Sec. III: the substitutional incorporation of Hf atoms in SiO_2 leads to stable configurations with strong but very localized relaxation patterns, with the interactions between nearest neighbors dominating the energetics.

Up to four **k** points were used for the Brillouin-zone integrations, as done in earlier studies.[6,13,15] The plane-wave cutoff was set at 400 eV (convergence was established by test calculations at 500 eV). This cutoff ensured well-converged formation and segregation energies. For all of the impurity configurations that we studied, all atoms were allowed to relax to their equilibrium positions during the course of the structural relaxation. The cell parameter along the interface-normal vector was also allowed to vary.

The formation entropies were calculated by using the method of Ref. 16, which is based on the local-harmonic approximation with the entropy determined as a sum of local (atomic) contributions. For a number of atoms, including the impurity itself and its surrounding neighbors (nearest-neighbor and second-neighbor shells), these contributions were obtained by diagonalizing the local dynamical matrices.

III. Hf IMPURITIES IN Si-SiO_2

Calculations were pursued for both substitutional and interstitial Hf across the entire Si-SiO_2 cell. Their formation energies were compared by using bulk Si to define the Si chemical potential, a choice suggested by the fact that Si is the element present in both sides of the interface. It was found that substitutional Hf in SiO_2 is lower in energy than interstitial Hf by 3–5 eV. This large difference arises because substitutional Hf is a very stable configuration with strong but rather localized relaxations of the surrounding O atoms restricted near the impurity. For the configuration depicted in Fig. 2(a), the four Hf-O bond lengths are in the range of 1.93–1.96 Å, namely, considerably longer than Si-O bond lengths in SiO_2 (~1.6 Å). These Hf-O distances are in agreement with an earlier work,[15] wherein the energetics of Hf impurities was reported for two sites near the Si-SiO_2 interface.

In contrast, interstitial Hf engages in extensive rebonding in the surrounding lattice, seeking to attain a fourfold coordination by pulling nearby O atoms. Two Si-O bonds break in the process, leaving behind undercoordinated Si atoms with dangling bonds. The lowest-energy interstitial configurations, at the interface and deep in SiO_2, are displayed in Figs. 2(b) and 2(c), respectively, with formation energies that are 4 and 5 eV higher than that of substitutional Hf deep in SiO_2. In these configurations, interstitial Hf atoms form two short Hf-O bonds (in the 1.92–1.98 Å range) with the O atoms that have been *pulled away* from the nearest Si atom. They also have two long Hf-O bonds with bond lengths in the 2.26–2.58 Å range, which are similar in magnitude to the Hf-O distances in bulk crystalline phases of HfO_2.[17] Although large relaxations imply higher entropies of formation,[18] the calculated entropy differences do not exceed $3k_B$, with the principal contributions originating from the Hf interstitial impurity ($1k_B$ higher than substitutional Hf) and the undercoordinated Si atom ($1.5k_B$). The explanation for such small differences in formation entropies should be attributed to the very strong tendency of interstitial Hf to attain an O fourfold coordination during the course of the relaxation. This leads to a similar *tight* local environment for Hf as in the substitutional case (in terms of actual Hf-O bond lengths) that restricts the Hf vibrations inside the large voids of the quartz lattice. Thus, the entropy contribution to the free energy difference is only 0.3 eV, even at 950 °C, the postdeposition annealing temperature.[5] The net conclusion is that interstitial Hf has a much higher free energy of formation than substitutional Hf. This conclusion can explain the extremely low Hf diffusivity in undamaged SiO_2:[9] diffusion of substitutional impurities in Si is normally mediated by pertinent vacancies or interstitials,[19] but in SiO_2 these defects have high energies because of the material's network structure (even if interstitial Si atoms were available, the high formation energy of interstitial Hf in SiO_2 would inhibit a kick-out diffusion mechanism for Hf).

The calculated formation energies of single substitutional Hf across the entire cell are shown in Fig. 3. Results for substitutional Zr and P atoms and P^+ ions were also obtained (ZrO_2 oxide is another alternative gate dielectric and P is a common dopant in Si). In each case, the zero of energy was taken when each impurity atom is located deep in the Si crystal. It is clear that substitutional Hf (and Zr) has the lowest formation energy deeper in the oxide, at least 4 Å away from the interface plane. That the behaviors of Hf and Zr are similar is not surprising: besides being of equal size, these elements possess the same type of nd^2-$(n+1)s^2$ electronic configuration in their outer valence shells. The energy for both Hf and Zr substantially rises at sites closer to the interface, with a large penalty (1.4 eV for Hf) for segregation to the interfacial plane. The entropy of Hf at the interface is $1.4k_B$ higher than that of Hf in the oxide, decreasing the free-energy difference between the two sites by only 0.14 eV, even at 950 °C. Therefore, there is no driving force for Hf segregation, at least when the Hf atoms are originating in the oxide side of the interface. This result also holds for the case wherein SiO_2 has a tridymitelike structure (similarly constructed; see Ref. 13). Again, the formation energy for substituting Hf impurities at the nominal Si interface plane is considerably higher (by 1 eV) with respect to that for substituting Hf at the two Si planes in the oxide adjacent to the Si-SiO_2 interface. In addition, we found that two Hf atoms inside the oxide avoid substitution at neighboring Si sites that share an O bridge; O-bridge sharing increases their energy by 0.8 eV. Thus, the theoretical results account for the *Z*-contrast observations that *Hf atoms in the* SiO_2 interlayer remain dispersed and stay away from the interface.

The present study also aims to contrast the segregation behaviors of Hf and dopants in the Si side of the interface. Hf atoms can be introduced in bulk Si by ion implantation in-diffusion as is the case for common dopants.[20] Figure 3 shows that the formation energy of a single substitutional Hf at the interfacial Si plane is a minimum relative to sites inside Si. This result suggests that if diffused in the Si substrate, substitutional Hf atoms would segregate to the interfacial plane and form two Hf-O bonds, as Fig. 3 illustrates. In addition to the above, we calculated the energy of interstitial Hf in Si and explored other segregation modes. Interstitial Hf is stable at tetrahedral sites with four Hf-Si bonds of 2.52 Å, which are slightly shorter than the Hf-Si bonds of substitutional Hf (2.59 Å). This configuration has localized states in the Si bandgap. Thus, there can be charged states of the interstitial with a formation energy that varies with the Fermi energy. Assuming bulk Si defines the Si chemical potential, we find that interstitial and substitutional Hf in Si have nearly equal formation energies. In contrast, Hf in the hexagonal interstitial sites is unstable (in the neutral state) and relaxations always lead to Hf finally occupying the tetrahedral interstices.

More importantly, however, pairs of substitutional Hf atoms in Si undergo substantial relaxations and lower their energy by almost 2 eV by forming interstitial pairs (see Fig.

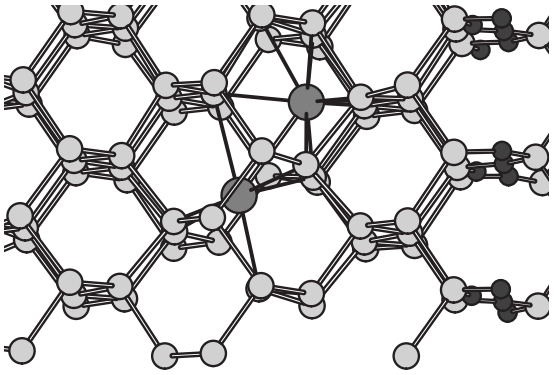

FIG. 4. Hf-Hf interstitial pair in Si.

4) with a Hf-Hf spacing of 3.28 Å, which is close to the nearest-neighbor spacing in Hf metal (3.13 Å).[21] Thus, Hf impurities may form clusters in bulk Si, something that can also be related to the fact that Hf (with a very limited solubility in Si) forms intermetallic compounds with Si where Hf-Hf bonds exist.[22]

This tendency for dimerization (and possibly clustering) has important implications to the segregation propensity of Hf atoms: the formation of Hf-Hf interstitial pairs in bulk Si with a strong binding energy will prevent them reaching the Si-SiO_2 interface, despite the fact that the segregation of single Hf impurities from the Si side to the interface is energetically very favorable (see Fig. 3). If isolated Hf atoms reach the interface, they would segregate at the interfacial Si plane, but they would not penetrate further into SiO_2 (even though Fig. 3 shows a further energy lowering) because of the lack of a diffusion mechanism. Inside Si, substitutional or interstitial Hf can diffuse by a vacancy or self-interstitial mechanism, just like dopants.[19] In the oxide, however, as we noted earlier, the network structure makes it impossible for Si vacancies to exist and mediate diffusion of substitutional impurities. Thus, the Si-SiO_2 interface can be regarded as a Hf diffusion barrier even though interstitial Hf atoms can exist in both sides of the interface.

IV. ORDERING NEAR THE INTERFACE

Having established that the Hf atoms observed in the *Z*-contrast images replace Si atoms inside SiO_2, we can view them *as markers for Si sites*. From the experimental data, we constructed a histogram of the number of Hf atoms versus the distance from the interface plane (see Fig. 5). The histogram clearly reveals that the Hf positions in SiO_2 are not random; rather, they are distributed at certain distances from the interface plane. Although there is *no* evidence for true crystallinity in the SiO_2 layer, ordering of *at least two* Si planes is present. Such "planes," of course, are not sharp, as atomic distances from the interface vary about a mean value; nonetheless, the data clearly indicate that there is an *ordered* transition region in the oxide (approximately 5 Å wide) that intervenes between the crystalline Si substrate and the amorphous SiO_2 interlayer. Similar observations of gradual structural ordering at crystalline amorphous interfaces were recently reported for Si-based ceramic materials.[23,24] In Fig. 5,

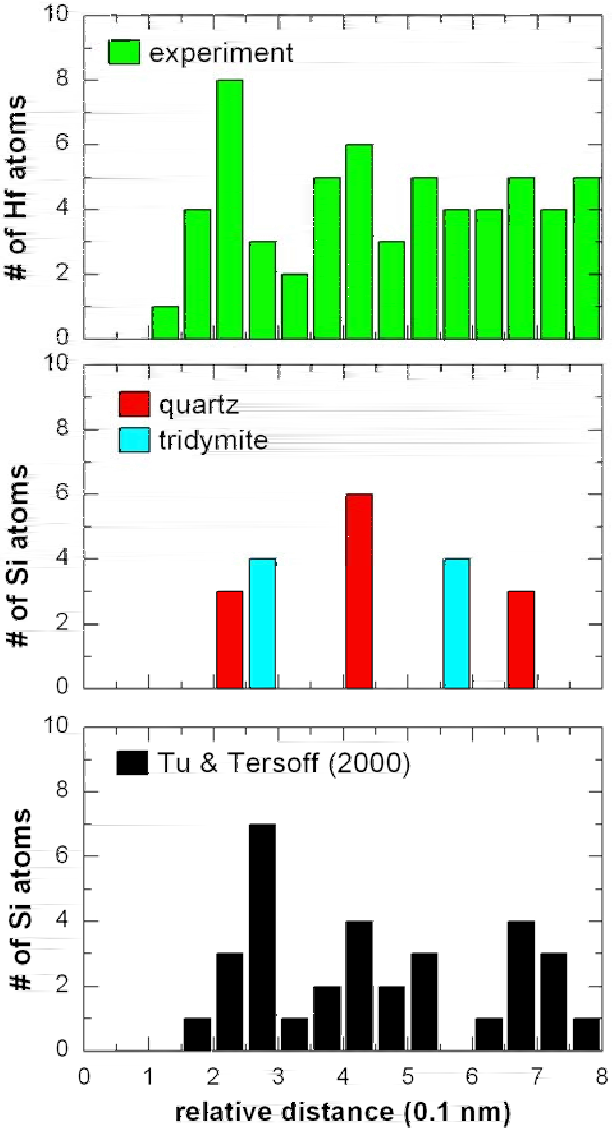

FIG. 5. (Color online) Histograms representing the number of Si atoms as a function of distance to the Si-SiO_2 interface plane as extracted from the experimental data set and determined for the theoretically derived structures.

we also show histograms of the Si sites in the quartzlike (see Figs. 2 and 3) as well as the tridymitelike structures employed in the present study. In addition, we compared these to the histograms obtained from model structures with amorphous SiO_2 reported by Tu and Tersoff[25] using the coordinates kindly provided by the authors. These model structures were determined from Monte Carlo simulations by performing bond-switching moves and approximating the energetics by empirical interactions.[25] Here, we show only the histogram for the model structure that closely resembles the experimental data. The experimental and model histograms exhibit good overall agreement, corroborating the conclusion about the presence of ordering in the amorphous SiO_2 layer near the interface. Notable differences, however, are still evident. In particular, neither a pure quartzlike nor a pure tridymitelike interfacial region (as proposed in a previous electron-microscopy study[26]) could capture the main features

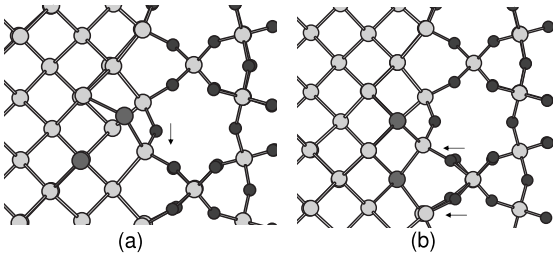

FIG. 6. Pair configurations of dopants at the subinterface region: (a) nearest-neighbor and (b) second-neighbor dopant pairs. The arrows denote displaced atoms.

of the experimental data. Furthermore, the model interfaces essentially have no Si atoms in a 2 Å wide region adjacent to the Si interfacial plane. In contrast, the experimental data reveal a number of Si atoms in this region. Thus, real Si-SiO_2 interfaces, although abrupt, may have a slightly more complicated structure than the three model interfaces of Fig. 5 would suggest.

V. DOPANT SEGREGATION

The segregation behavior of dopants in Si, on the other hand, is distinctly different from that of Hf, as the results of substitutional energetics (plotted in Fig. 3) have already indicated. Dopants are known to diffuse in Si with the aid of vacancies or self-interstitials[19] and can eventually segregate to the Si-SiO_2 interface. The calculated formation energies of a single substitutional P (Fig. 3) suggest that P does not segregate to the interface plane, where P-O bonds are energetically very costly, in agreement with previous results.[27,28] Instead, segregation is predicted to the subinterface Si plane with a small energy gain (0.16 eV). We also found that segregation of two isolated P dopants on this plane is always preferable against pair formation. However, pair formation near the interface (see Fig. 6) is preferable with respect to dissociation into two isolated dopants *in bulk Si*. Gaining energy by pairing was first proposed within the context of As segregation in Si grain boundaries[29] and dislocations.[30] Pair formation is driven by the tendency of neutral dopant atoms to establish their preferred threefold coordination as in PH_3 and AsH_3 molecules. Pairing was also later suggested[27,28,31] to occur at the Si-SiO_2 interface in order to explain the observed dopant pile up for higher implanted doses.[27] We found that a nearest-neighbor P-P pair just below the interface plane lowers its energy (by 0.23 eV with respect to two isolated P dopants) by breaking the P-P bond (P-P distance of 3.28 Å) and achieving a threefold coordination for the two dopant atoms [Fig. 6(a)]. In this configuration, one of the dopants is displaced from its initial Si lattice site toward the available interstitial region closer to the interface. This relaxation pattern appears to be accommodated by the near-interface oxide region, in particular, the displacement of the O-bridge atom connecting the Si atoms of the nominal interface plane [see Fig. 6(a)]. Again, even as pairs, P atoms avoid sites where there is a possibility to form P-O bonds. Thus, *segregation occurs in the Si side of the interface* in the subinterface region (experimental evidence on this issue has been conflicting[3,4]).

Furthermore, second-neighbor P-P pairs [see Fig. 6(b)] and pairs of larger P-P separations may also be stabilized in the subinterface plane. Such pairs do *not* entail a threefold coordination. The energy gain arises from relaxations of the near-interface oxide network [as depicted in Fig. 6(b), two O-bridge atoms are displaced toward the Si substrate by 0.2 Å], a fact that previous computational studies[27,28,31] of dopant segregation to the Si-SiO_2 interface overlooked. The binding energy for this pair is 0.15 eV (with respect to two isolated P atoms in bulk Si). We want to point out here that, although these segregation enthalpies for the dopants are quite small, the corresponding entropy differences are even smaller (less than $0.5k_B$, which yields less than 0.05 eV at 950 °C), so that our conclusions remain true. Similarly, As dopants were found to segregate as single impurities at the subinterface Si plane. However, pair formation was only found preferable (with respect to two As dopant atoms isolated in bulk Si) for the nearest-neighbor pair geometry.

It is also interesting to note that dopant pairs in bulk Si have a negligible binding energy with respect to dissociation into two isolated dopant atoms. Therefore, in contrast to Hf, dopant-dopant coupling can lead to stable configurations only near the Si-SiO_2 interface.

VI. CONCLUDING REMARKS

The overall conclusion from the present study is that impurities (either single or pairs) may or may not segregate to the interface depending on their chemical identity and on which side they come from. For the specific system studied here, both the calculations and the experimental data demonstrate that there is no driving force for segregation when Hf atoms are initially located in the SiO_2 layer. Similarly, a tendency for interstitial-pair formation inside Si will inhibit Hf segregation from the Si side. Group-V dopants in Si only segregate to the subinterface region either as single impurities or by forming pairs that do not necessarily entail a threefold coordination as previously thought.[27,28] Relaxations in the oxide close to the interface that are not costly in elastic strain energy were found to facilitate dopant segregation.

Finally, the present synergistic approach by *Z*-contrast imaging and density-functional calculations strongly indicates the presence of ordering in a narrow 5 Å wide region in the oxide adjacent to the interface, whose detailed structure still remains unidentified.

ACKNOWLEDGMENTS

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