Mechanism of dopant segregation to SiO_2/Si(001) interfaces

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Dopant atoms can segregate to SiO_2/Si(001) interfaces and be deactivated there. Using phosphorus as a typical example of a donor and guided by results of *ab initio* calculations, we present a model of donor segregation. We find that P is trapped at the interface in the form of threefold-coordinated atoms. The atomic detailed configuration and the process of P incorporation depend on P concentration C_P in the vicinity of the interface. At low C_P, phosphorus atoms prefer to substitute Si atoms with dangling bonds. At high C_P, phosphorus pairs are formed. At intermediate C_P, (around 10^{17}–10^{19} cm^{-3}) segregation occurs to sites associated with interface roughness and to interface Si-Si bridges, and is mediated by diffusion and annihilation of Si dangling bonds and by reoxidation during oxide annealing. Making diffusion of dangling bonds more difficult (for example, by nitridation) should, therefore, reduce the trapping efficiency of SiO_2/Si(001) in the technologically important regime of intermediate C_P.

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I. INTRODUCTION

Silicon MOS (metal oxide semiconductor) technology is a versatile, inexpensive, and widely used method of fabrication of microelectronic integrated circuits. Electrical parameters of a MOS field effect transistor (MOSFET) are sensitive to the spatial distribution of dopant atoms in the active region of the device. The design of technological processes needed to produce a chip must account for all factors that may significantly affect this distribution. In MOSFET's, SiO_2 is placed next to doped regions of the silicon substrate.[1,2] Segregation to SiO_2/Si(001) interfaces can cause redistribution of dopants during the fabrication process, an effect that becomes significant in "decanano" devices[2–5] and can affect the MOSFET threshold voltage (the voltage at which the transistor switches) by up to 50%.[6]

SiO_2/Si(001) interface is an efficient trap for donors. It can collect at least $3\times10^{14}/cm^2$ P atoms,[7] an amount close to a monolayer (ML); for Si(001), 1 ML$=N_o\simeq7\times10^{14}/cm^2$. Majority of the trapped atoms are located on the Si side in the first monolayer of silicon.[8–10] The atoms trapped at the interface are deactivated,[9] which means that they are not shallow dopants. The segregation process is partially reversible by subsequent annealing at temperatures higher than the temperature at which the atoms segregated.[7,11,12] It is interesting to note that also interfaces between Si and a chemically prepared SiO_2 film exhibit a similar segregation behavior as interfaces with thermal oxides.[13] The same is true for interfaces between Si and buried SiO_2 layers.[14]

How do the dopant atoms arrive at the interface? First, they diffuse through the silicon, mostly with help of point defects[15–17] introduced during dopant implantation.[2,18] Alternatively, they may be "shovelled" by the moving (oxidizing) SiO_2/Si interface during thermal oxidation of the substrate.[8,9,19]

Segregation models used in complementary metal-oxide semiconductor technology process simulation assume that the interface has approximately 1 ML of unspecified dopant traps.[11,20–22] The nature of these traps is unknown. It is also unclear why the segregated atoms do not act as shallow donors. A possible explanation is that complexes between donor atoms and Si vacancies are formed at the interface;[9] this would mean that the segregation to SiO_2/Si interfaces is a process similar to segregation to bare surfaces of silicon. Elastic stress relaxation[23] and Fermi-level effects[9] have also been suggested as forces driving the segregation.

The purpose of this work is to shed some light on such issues, given the atomistic data obtained from total energy *ab initio* calculations. We have attempted to connect these data into a set of microscopic mechanisms building a "complete" segregation story. Naturally, this story should be viewed as an educated guess rather than a proven segregation process, and experimental verification of its key ingredients would be desirable. So far, our observations confirm that Fermi-level position at the interface and the ability of certain atomic configuration to relax the elastic stress between the oxide and the substrate are the key factors in the segregation mechanism. We also find some *ab initio* justification for the supposed importance of Si vacancies in donor trapping at the interface.[9]

In our previous work we have already formulated a tentative segregation model based on *ab initio* numerical results for P and As.[24,25] Comparison of the numerical results with experimental secondary-ion-mass spectroscopy (SIMS) data revealed[24] that there are three fundamental regimes of P concentration C_P characterized by three different interface adsorption mechanisms dominating the segregation. At very low C_P, the donors arriving at the interface substitute undercoordinated Si atoms (Si atoms with dangling bonds). This is analogous to segregation of dopants to Si surfaces.[26] At very high C_P, the dopants form pairs of electrically neutral, threefold-coordinated atoms, analogous to DX and EL2 instabilities of donors in GaAs.[27] The segregation mechanism

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at intermediate C_P, where dopants are trapped as individual atoms but the density of traps exceeds the density of dangling-bond sites, has not been identified. In all cases, however, we found that the formation of donor-oxygen bonds is energetically unfavorable, in agreement with experimental data.

Here we focus on atomistic details of the segregation process in the regime of intermediate donor concentrations. In addition, theoretical results for the other two C_P regimes are summarized and extended. In particular, we identify dopant pairing by silicon ejection as a process that may compete with the other pairing mechanisms.

The paper is organized as follows. Section II explains the theoretical and experimental approaches. Section III discusses various atomistic segregation mechanisms. Section IV presents the segregation model associating the areal density D_P of phosphorus trapped at the interface with the annealing temperature and the concentration C_P of shallow P donors under the interface.

II. APPROACH

Ab initio calculations[28] were performed on a Cray T3E supercomputer in von Neumann Institute for Computing, Jülich, Germany. We used supercells of Si(001) type, with lateral dimensions from 2×2 to 4×4(measured in translation vectors of the ideal surface). Vertically, the supercells contained six to eight Si layers and one to three oxide layers. The slab was saturated with H atoms. Coordinates of the H atoms saturating the Si substrate slab were computed by energy minimization of Si(001) 1×1-H surface with all Si atoms confined to their bulk positions. These saturating H atoms and their Si neighbors were frozen in their positions during all subsequent relaxations of the system. The chemical potential of each donor species (P, As) was calculated from the total energy of a substitutional donor atom in the third or fourth Si layer below the interface in a 4×4 supercell. The chemical potentials of Si and H were obtained from the dependence of H-saturated slabs on the number of Si layers in the slab. The chemical potential of oxygen in SiO_2 films was calculated assuming thermodynamical equilibrium between Si atoms in the film and in the substrate.

Numerical convergence was verified by performing test calculations at plane-wave cutoff energies between 16 Ry and 50 Ry and with Brillouin zone sampling equivalent to Γ and (1/4,1/4) points of 2×2, 3×3, and 4×4surface cells. The data quoted below were obtained using 40 Ry cutoff and the Γ point of 4×4. The estimated numerical uncertainty in energy differences is about 0.2 eV per cell due to Brillouin zone sampling and the energy cutoff. Additional uncertainty of approximately 0.1 eV per atom exchanged with a reservoir enters through inaccuracies in the calculation of chemical potentials. Although the energy differences calculated to be around 0.2–0.3 eV may still have physical significance (numerical errors tend to cancel out when energies of similar atomic configurations are compared), the differences smaller than about 0.1 eV will be considered in this paper as negligible.

Reliability of the results was also checked through comparison with electronic structures and energy differences for test Si-P, Si-O, and Si-O-P structures in bulk silicon computed with other *ab initio* codes[34] and, in the case of the Si vacancy in the bulk and under the interface, with energy differences obtained by a semiempirical method [AM1 (Ref. 38]. The compared values were within the 0.2–0.3 eV error bar, confirming our estimate of the numerical accuracy.

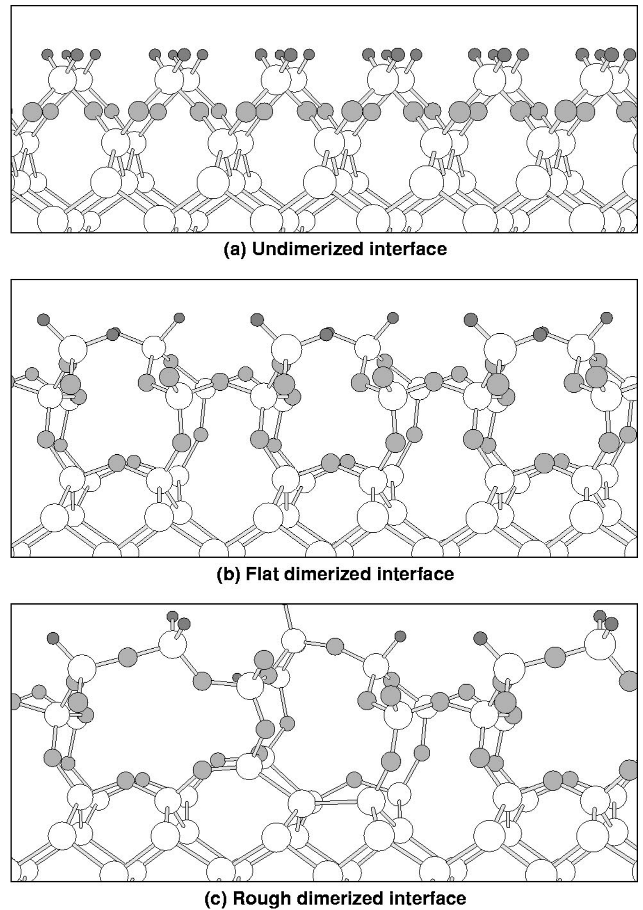


FIG. 1. Interface models. (a) Undimerized interface. (b) Flat, dimerized interface with tridymitelike SiO_2. (c) Rough, dimerized interface.

In order to make the calculations feasible for many interface structures, the SiO_2/Si(001) cells were designed to represent the key features of the interface with possibly few atoms. Undimerized [Fig. 1(a)] and dimerized interfaces [Fig. 1(b)] were considered. In an undimerized interface, a layer of SiO_2 was attached through oxygen atoms to Si(001) 1×1surface. In dimerized interfaces, up to three layers of tridymite-based SiO_2 were attached through oxygen atoms to Si(001) 2×1 surface with oxidized dimer bonds. A rough interface was simulated by introducing *D*-type ad-dimer rows[37] in 4×2cells [Fig. 1(c)].

Binding energies of donors under SiO_2/Si(001) were studied by substituting P for Si atoms in the substrate at various distances from the SiO_2/Si(001) boundary. Segregation to dangling-bond sites was addressed by replacing unsaturated Si atoms at SiO_2/Si(001) boundaries. Formation of complexes containing one or more donor atoms and/or a point defect was studied in Si bulk and under the interface.

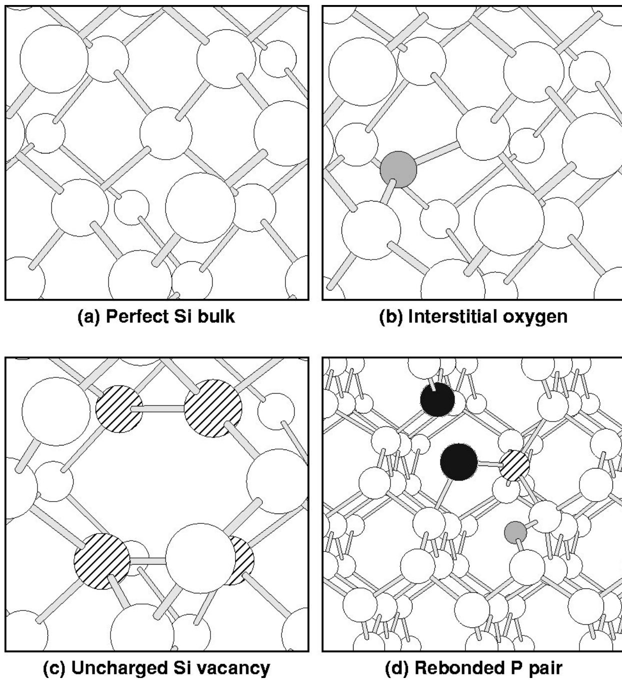


FIG. 2. Configurations of selected bulk structures. Si atoms are white, O atoms are gray, P atoms are black. (a) Perfect Si. (b) O_i, oxygen interstitial. (c) Uncharged Si vacancy; the dimerized atoms are dashed. (d) Rebonded P pair. The dashed Si atom and its P neighbor are {113} rebonded,[26] the other P atom stays in a nearly substitutional position.

The bulk defects included a nearest-neighbor P pair (P_2), oxygen interstitials [O_i, Fig. 2(b)), Si vacancies [V_{Si}, Fig. 2(c)] complexed with P and O_i (e.g., the AP_2 center[24]), and rebonded defects $113Si_2$ and $113P_2$ O_i [Fig. 2(d)]. Segregation to interface sites with an unoxidized Si atom was investigated for a Si vacancy, a Si bridge, and a Si ledge atom. Diffusion of a Si dangling bond was studied for the dangling bond created after a P atom was incorporated into a step ledge. We estimated the height of the diffusion barrier by computing total energies at the energy minima and for several atomic configurations near the top of the barrier. In the latter case, the motion of one oxygen atom was constrained to a plane and the remaining atoms were relaxed.

Auger electron spectroscopy (AES) data were collected through native oxide layers thin enough (~ 15 Å) to make the interface P observable. In order to minimize electron-irradiation effects, the spectra were taken at low primary electron-beam energy and current density.

III. SEGREGATION MECHANISMS

Experimental data indicate that moving a donor atom from the silicon bulk to the interface releases about 0.5–1.0 eV. Since trapping of donors does not deteriorate electrical properties of the interface, the segregation mechanism cannot be correct if it leads to excessive creation of electrically active defects. Moreover, the segregated atoms should not act as shallow donors.

First, we investigate the energetics of P atoms in the silicon substrate close to the SiO_2/Si(001) interface (Sec. III A) and P atoms substituting oxidized Si atoms directly at the interface (Sec. III B). Next, we analyze P trapping by substitution of unoxidized Si at atoms with a dangling bond (Sec. III C) and at unoxidized fourfold-coordinated Si in interface defects (Sec. III D). The latter process includes diffusion of Si dangling bonds along the interface. Finally, we consider the formation of donor-donor pairs (Sec. III E).

A. Substitutional donor atoms under the interface

In principle, one can imagine that deformation of Si-Si bonds caused by strain fields in the oxide attracts phosphorus to the interface and localizes the fifth valence electron of P in a deep state. We find that substitutional phosphorus P_{Si} may be weakly bonded ($\lesssim 0.2$ eV) in the second Si layer beneath a perfect, undimerized interface. As the first layer we count here the topmost Si atoms of the substrate, connected in such an interface to two Si atoms on one side and to two oxygen atoms on the other side [Fig. 1(a)]. Interestingly, it turns out that atomic relaxation around P contributes little to this binding. The energy gained when the impurity neighbors relax from their positions they had occupied before the Si atom was substituted by the P atom is about the same in the bulk and under the interface. Therefore, this weak interaction is probably not caused by interface strain.

In our opinion, the binding arises from hyperconjugation between the fifth valence electron of phosphorus and antibonding orbitals of silicon atoms from the first layer of the substrate. This type of interaction formally resembles hydrogen bonding and is responsible for such effects as planar configuration of N in Si_3N_4(interaction between the lone pair of N and antibonding orbitals of Si) and the low formation energy of Si monomers on Si(001) surfaces (interaction between the lone pair of Si monomer and antibonding orbitals of subsurface Si). Hyperconjugation between P and Si at the interface is noticeable because the fifth electron of phosphorus is partially localized in a conduction-band resonance and Si orbitals are partially emptied due to charge transfer from silicon to oxygen. The strength of this interaction increases with the oxidation number of silicon and decreases with the number of P neighbors of the oxidized Si atom. Binding by hyperconjugation is opposed by the electrostatic force that repels the positively charged silicon from phosphorus ions. Virtually no binding was found in deeper layers, regardless of the interface structure. This is consistent with the interpretation of the interaction between P_{Si} and a SiO_2/Si boundary presented above.

The weak attraction of P to undimerized interfaces appears to be the upper limit for the binding energy of P_{Si}. Depending on the structure of the interface, we find either a weak binding or a weak repulsion when P is placed in the second Si layer. However, in all cases the energy difference between the impurity in the bulk and the impurity under the interface does not exceed 0.2 eV, which is less than the estimated numerical accuracy.

Formation of a coherent silicide (SiP in the zinc-blend structure) also leads to no significant energy gain. We conclude that neither the attraction of substitutional donors to

the interface nor the decreased solubility of P due to enhanced silicide formation under the interface is the dominant mechanisms for dopant segregation. Although we cannot disregard the fact that these effects exist, we believe that other atomic geometries, for which we find higher binding energies, are responsible for the segregation.

B. Bonding of donors to oxygen atoms

All structures with P-O of As-O bonds were unstable or nearly unstable with respect to exchange of the oxidized donor atom with a Si atom in the substrate. This includes defect complexes formed in the bulk Si as well as interfacial structures. The energy difference by substituting a single oxidized silicon atom by a group-V donor was about $E_{o1n4}=(0.5\pm0.2)$ eV (energy loss) when the oxidized atom was fourfold-coordinated and about $E_{o1n3}=(-0.1\pm0.3)$ eV (energy gain) for a threefold-coordinated oxidized atom. We conclude that atomic geometries with donor-oxygen bonds play no important role in the segregation of P.

These results are in accordance with our AES data obtained through native oxide. The detectable P is elemental. We found the P_{LVV} peak at 120 eV, which coincides with the position of uncharged P and is $\sim$10 eV higher in energy than the P peak in P_2O_5.[39] The identification of the observed spectral line as due to unoxidized phosphorus is corroborated by the fact that electron-beam-induced evaporation of the oxide affected neither position nor shape of this line. This is consistent with the known fact that P is expelled from SiO_2 during thermal oxidation of Si.[40] It follows that the state of segregated P differs from the states of P donor and oxidized P: the latter are positively charged, whereas the segregated P atoms are electrically neutral. This result allows us to argue that a monolayer of efficient P traps is unlikely to exist at the interface, because P atoms bonded at such traps would have oxygen neighbors.

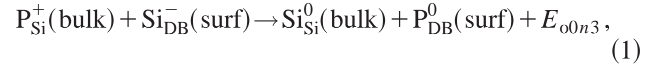
On the other hand, it is known that interfaces to native oxides contain much higher concentration of electrically active defects (presumably Si dangling bonds) than interfaces to thermal oxides used as MOSFET gate dielectrics.[41] These concentrations are $\sim10^{13}/\text{cm}^2$ and $\sim10^{12}/\text{cm}^2$, respectively. As noted below, such dangling bonds are the preferred segregation sites. Our experiment confirms that the most efficient trapping does not involve formation of P-O bonds. However, it does not exclude that interfaces with thermal oxides may contain sites at which P atoms bonded to O reside after many dangling-bond sites have been occupied.

Finally, we note that the value of E_{o1n3} is small enough to be compatible with the small but observable incorporation of P from the substrate into SiO_2. The equilibrium ratio of P concentration in SiO_2 and Si is approximately 10%,[21] which corresponds to the binding-energy difference of $\sim$0.2 eV at temperatures around 800–1000 °C.

C. Si dangling bonds

Segregation of donors to silicon surfaces is a known and easily understandable effect. For a group-V atom it is more convenient to occupy a threefold-coordinated site on the surface of a group-IV semiconductor, where it can be electrically neutral, than to substitute a fourfold-coordinated in the bulk crystal, where its fifth electron must be donated to conduction-band states. For a group-IV Si atom it is also more convenient to have all valences saturated in the bulk than to have its fourth electron forced into a virtually open-shell configuration on the surface. In the same vein, it is known that defects that contain undercoordinated Si atoms or weak Si-Si bonds, such as Si vacancies [Fig. 2(c)], act as efficient phosphorus or arsenic traps. By analogy, one expects that undercoordinated Si atoms left in the SiO_2/Si(001) interface after oxidation will be the preferred sites for donor segregation.

Indeed, reactions in which a phosphorus atom substitutes an undercoordinated, unoxidized Si atom,



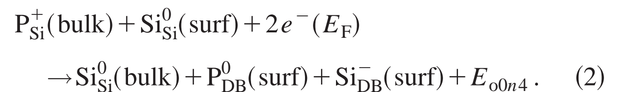
$$P_{Si}^{+}(\text{bulk})+Si_{DB}^{-}(\text{surf})\rightarrow Si_{Si}^{0}(\text{bulk})+P_{DB}^{0}(\text{surf})+E_{o0n3}, \tag{1}$$

are exothermic. The energy of a positively charged substitutional P_{Si}^{+} in bulk Si and a negatively charged Si dangling-bond Si_{DB}^{-} on the surface is higher than the energy of an electrically neutral P_{DB}^{0} occupying a triple-coordinated site on the surface, because in the latter case all Si atoms and all P atoms are uncharged. In addition, the reaction (1) transforms one Si-P bond into one Si-Si bond. The computed energy gain is $E_{o0n3}\simeq1.1$ eV. However, there is no noticeable energy gain when the substituted atom is oxidized (Sec. III B).

Given their high binding energy for phosphorus, the interface Si dangling-bond sites might seem to be the defects responsible for the segregation. However, a Si dangling bond is electrically active. Even low-quality SiO_2/Si(001) interfaces have much fewer electrically active defects than the number of dangling-bond sites needed to adsorb about a monolayer of donors. In interfaces produced routinely by industrial-quality oxidation no more than several Si atoms in a thousand have a dangling bond (this is further reduced by a factor of about a 100 by postoxidation annealing in hydrogen). Nevertheless, even in such good interfaces the effective concentration of P traps is approximately one monolayer. This means that Si dangling bonds cannot be the major traps, at least when the total amount of segregated donors exceeds about $10^{12}/\text{cm}^2$ (thermal oxide before hydrogen passivation) or $10^{13}/\text{cm}^2$ (native oxide).

D. Defects with unoxidized Si

Other defects that might potentially act as traps for phosphorus are interface defect sites containing an unoxidized and fully coordinated Si atom. These are: silicon bridge [Fig. 3(a)], a ledge atom of an interface step [Fig. 3(b)], or a silicon vacancy (Fig. 3, bottom panels). Consider a reaction of type



$$P_{Si}^{+}(\text{bulk})+Si_{Si}^{0}(\text{surf})+2e^{-}(E_F)\rightarrow Si_{Si}^{0}(\text{bulk})+P_{DB}^{0}(\text{surf})+Si_{DB}^{-}(\text{surf})+E_{o0n4}. \tag{2}$$

This reaction transforms a fourfold-coordinated P_{Si} ion into a threefold-coordinated, electrically neutral atom. The transformation comes at a price: a dangling bond is created at the

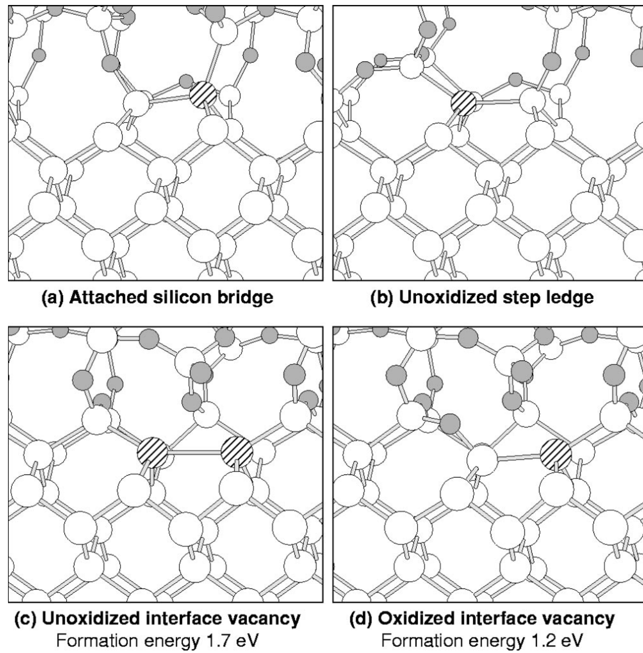


FIG. 3. Defect sites containing an unoxidized and fully coordinated Si atom. The unoxidized atoms in the defects are dashed. (a) Silicon bridge. (b) Step ledge. (c) Unoxidized interface vacancy (high formation energy of 1.7 eV). (d) Oxidized interface vacancy (low formation energy of 1.2 eV).

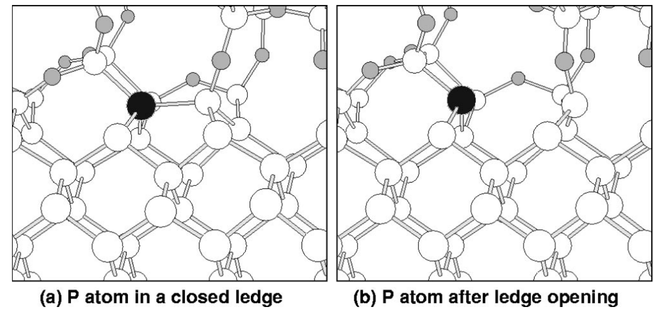


FIG. 4. Segregation to an unoxidized step ledge site: dangling-bond creation phase. (a) P atom in a closed ledge dimer. (b) P atom and a Si dangling bond after ledge opening.

interface. We will now discuss the energetics of such processes. We will also argue that this mechanism is consistent with the experimental observation that donor segregation is not accompanied by excessive generation of electrically active defects. We will see that such trapping is energetically favorable because the dangling bonds produced in reactions described by Eq. (2) are annealed out and/or oxidized during the same thermal processing that leads to segregation of donors.

Si vacancies are an interesting candidate for trapping centers because it is known that they are produced during dopant implantation and accumulate under the surface. The key question is: how many Si vacancies can exist in thermal equilibrium at and directly below the interface?

We estimated that the binding energy of a single, electrically neutral V_{Si} under the interface is ~ 1 eV when the vacancy site is in the second layer of the substrate. The binding increases by additional 0.5–1.0 eV [Fig. 3(c) and 3(d)] when the vacancy site is in the interface layer. The vacancy is attracted to the layer under the interface because there it can profit from facilitated relaxation of its elastic stress field (caused largely by dimerization of the vacancy neighbors); similarly, the presence of a void under the interface facilitates relaxation of the stress in the interface layer (caused largely by different bond angles preferred in SiO_2 and in silicon). The additional binding of the vacancy directly at the interface is caused by a structural change of the defect. In its unreconstructed geometry, a bulk or sub interface V_{Si} has four Si dangling bonds surrounding the removed Si atom [these dangling bonds transform into two weak dimer bonds when an electrically neutral vacancy is allowed to relax, as in Fig. 2(c)]. In contrast to that, the unreconstructed geometry of an interface V_{Si} has only two Si dangling bonds. The other two Si neighbors of the vacant site are in the oxide. They are connected by an oxygen atom and do not induce any additional stress field. In a neutral V_{Si} at the interface, the two Si neighbors in the substrate form a weak dimer bond [Fig. 3(c)], so that the reconstructed vacancy has no dangling bonds.

Ab initio formation energy of uncharged V_{Si} is ~ 3.1 eV in bulk silicon. The binding energy of ~ 2 eV computed for a vacancy adsorbed at the interface means that the formation energy of a single interfacial V_{Si} is $\gtrsim 1$ eV. This value is too high to make such vacancies responsible for segregation of considerable amount of phosphorus. In thermodynamical equilibrium at temperatures 800–1000 °C, the formation energy of 0.8–1.0 eV corresponds to approximately one defected site per 10 000 atoms. A significantly lower formation energy would be required to achieve a sufficient concentration of defects at the interface in thermodynamical equilibrium. For example, one defect per 100 atoms corresponds to the formation energy of roughly ~ 0.4 eV. It seems that this energy differs from the computed value of $\gtrsim 1$ eV by more than the uncertainty due to our approximations and to the limited number of vacancy configurations we considered.

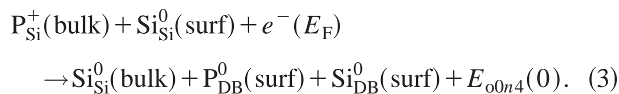
Nevertheless, we verified that P trapping at a single V_{Si} defect segregated to a dimerized interface is energetically favorable. The corresponding energy gain amounts to 0.7 ± 0.2 eV for the high-energy vacancy structure displayed in Fig. 3(c), even though a Si dangling bond is created in the process. The configuration with the dangling bond is energetically favorable because the Si-Si dimer bond of the vacancy was weak. Unfortunately, weakness of such dimer bonds is responsible also for the high formation energy of the interface vacancy shown in Fig. 3(c) and, consequently, for very low concentration of these defects in thermal equilibrium. It follows that while the trapping activity of interface V_{Si} with weak dimer bonds is hindered by low concentration of these defects, the activity of interface V_{Si} with strong (relaxed) dimer bonds would be hindered by low energy gain or even energy loss due to creation of dangling bonds.

Indeed, the energy released when a phosphorus atom substitutes a Si atom in a relaxed Si-Si dimer bond, for example, in an interface step [compare Figs. 1(c) and 4] is small, or zero. The reaction (2) for such defects is barely favorable,

with $E_{o0n4}=0.2\pm0.3$ eV at $E_F=0.8$ eV. A dimer bond of this type is relatively strong; breaking it costs more than 2 eV. This is comparable to the bond strength in bulk Si [the LDA Si-Si bond energy is 2.6 eV (Ref. 45)]. As a matter of fact, it is difficult to compute the energy needed to break the ledge dimer bond because there is no barrier for recombination of the broken bond when the opened Si ledge is uncharged. Such a barrier appears when the defect traps an electron; the quoted value of 2 eV was computed for the atomic configuration of the metastable (i.e., broken-bond) geometry of the negatively charged defect.

The reaction (2) can be, however, the initial step in the process of phosphorus segregation. If the interface can reorganize itself in such a way that the dangling bonds created in the process described by Eq. (2) disappear and the energy barrier involved in this reorganization is small, then the P atom will be immobilized in the interface. The final state of the segregation reaction should in this case be the configuration in which the dangling-bond Si_{DB} recombines with another dangling bond to form a Si-Si bond, most probably a silicon bridge in SiO_2. A direct calculation of the energy gained by annihilation of this dangling-bond pair would require relaxation of interface structures with cells of lateral dimensions larger than 4×4, a task beyond our computational abilities. Instead, we estimate this energy by approximating the final state in several independent ways.

At first we assume that the recombination of the dangling bond produces a silicon bridge with the energy equal to the energy of the ledge dimer bond. In other words, we assume that recombination of two dangling bonds, created in the course of reaction (2) but *electrically neutral*, releases 2 eV. In order to use this recombination energy in the energy balance, we have calculated the energy of the reaction,



$$P_{Si}^{+}(\text{bulk})+Si_{Si}^{0}(\text{surf})+e^{-}(E_F)$$
$$\rightarrow Si_{Si}^{0}(\text{bulk})+P_{DB}^{0}(\text{surf})+Si_{DB}^{0}(\text{surf})+E_{o0n4}(0). \quad (3)$$

The dangling bond created in this reaction is electrically neutral. We need this because the reconstructed Si bond is also electrically neutral. Note that reaction (3) does not represent a real process; we simply use it as a measure of the energy of an uncharged dangling-bond energy before the recombination. The computed value of E_{oon4} is -0.4 eV (the minus sign indicates that energy is lost, i.e., work has to be done). From this we obtain the result that after the dangling bonds recombine, the segregation of a P atom from bulk Si to an unoxidized step ledge produces the energy gain of $2.0/2-0.4=0.6$ eV.

Second, we approximate the final state by the geometry shown in Fig. 5(a). This state differs from the intermediate configuration [Fig. 4(b)] in that the silicon with the dangling bond is now substituted by a P atom, so that no dangling bonds are left in the system and two P atoms have segregated. In addition, the oxygen atom that had connected the substituted Si atom with the oxide is now removed, so that no P-O bonds are created. Assuming that the oxygen atom is moved to the reservoir of oxygen atoms with energy equal to the average energy of oxygen in the SiO_2 film, we compute

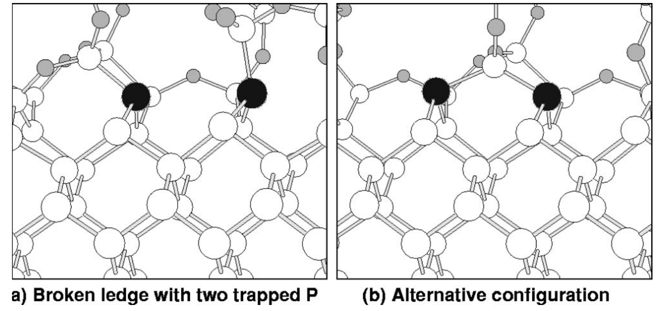


FIG. 5. Approximations to final state of P segregation: (a) Broken ledge configuration. (b) Alternative ledge configuration opening.

in this way that the energy gained by segregation of two P atoms from P_{Si} sites to the interface is 0.8 eV, that is, 0.4 eV per P atom.

The latter value of the segregation energy is relatively small because the geometry of Fig. 5(a) has a signifcant strain built into it. Namely, the angles between substrate Si-Si bonds and each of the two Si-P backbonds of the P atom substituting the Si atom with the dangling bond are far from optimal. This is improved in the geometry of Fig. 5(b). When such a configuration is assumed as the final state, the segregation energy increases to 0.5 eV per P atom.

Therefore, our estimate for P segregation energy to electricaly inactive, unoxidized Si defect sites at the interface is $E_{o0n4}=0.5\pm0.3$ eV at $E_F=0.8$ eV. This energy is much smaller than the energy gained by trapping at dangling-bond sites ($E_{o0n3}=1.1\pm0.2$ eV, Sec. III C), because in addition to the energy balance of the latter process, one Si-Si bond is effectively removed. Note that this additional energy cost [1.3 eV within local-density approximation (LDA)] would compensate or even overcompensate the energy gain E_{o0n3} if no energy gain other than that responsible for segregation of P to dangling-bond sites were involved. The supplementary gain comes from two sources. First, an electron is localized from the Fermi level to a localized site. This brings about (0.2–0.3) eV for $E_F=0.8$ eV (the difference between the energy of the midgap dangling-bond state and the effective energy of a delocalized electron). The remaining energy gain of (0.5 ± 0.6) eV comes from relaxation of the strain in the interface when the density of strained bonds connecting the film and the substrate is reduced; the error bar is obtained from the worst-case analysis. This gain is somewhat larger than in the similar case of donor pairing (Sec. III E) because strain relaxation when bonds are removed from the interface is more efficient than when the bonds are removed from under the interface.

Does this segregation indeed proceed independently for each P atom, or should one rather speak of correlated trapping of two P atoms? Since this mechanism involves recombination of dangling-bond pairs, its efficiency may be limited by the recombination speed and/or dissociation of Si bridges. If the dangling bonds do not diffuse fast, or if the concentration of Si bridges is controlled by the dangling-bond creation rate and not by the oxidation rate,[46] then the segregation rate and the dangling-bond creation rate become correlated. In

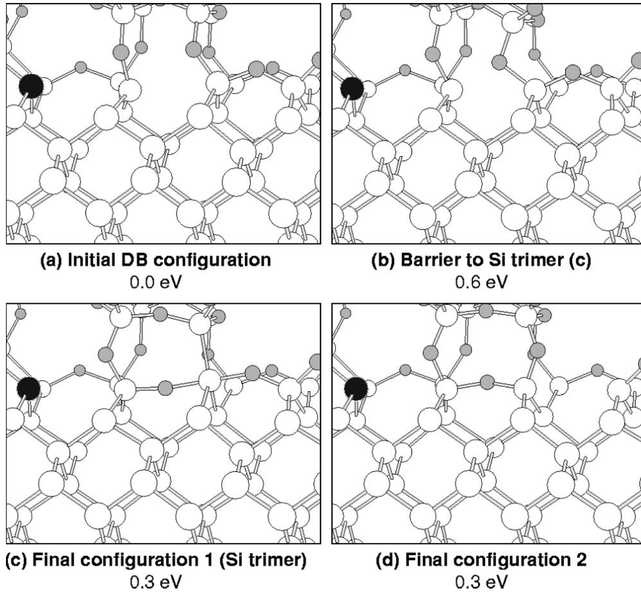


FIG. 6. Atomic configurations on dangling-bond (DB) diffusion path. (a) Initial configuration: DB created in reaction (2). (b) Barrier configuration on oxygen switching from SiO_2 to the Si atom with DB. (c) Switching complete: the DB in the oxide interacts with the mid-Si atom of an oxidized trimer in substrate. (d) Dangling bond moved to next dimer row.

this case, the segregation can be no longer treated as a process taking place independently for each P atom. Instead, it effectively becomes a pairing process (Sec. III E). Such processes are efficient only at high dopant concentrations (Sec. IV).

We verified that dangling bonds can diffuse fast along the interface. The diffusion barrier along the path indicated in Fig. 6 does not exceed about 1 eV, which is less than the activation energy of dopant diffusion in silicon. The barrier for dangling-bond migration is low because SiO_2 network can be easily deformed. An oxygen atom can easily rotate along the axis connecting its Si neighbors, and it can easily move so close to the dangling bond that a Si-O bond switches smoothly between one of the neighbors of the moving oxygen and the Si atom that had the dangling bond. In this way, the dangling bond flows across the network without too much resistance.

Furthermore, it is known that segregation of phosphorus is stronger in more oxidizing ambients.[2] This is compatible with our assesment that Si bridges are involved in the segregation process: less oxidation means more bridges, hence a higher bridge dissociation rate, hence a higher concentration of dangling bonds in the oxide, hence a higher rate of the association reaction reverse to the reaction (2) and, consequently, a lower concentration of trapped, threefold-coordinated P atoms.

E. Dopant pairs

Trapping on interface dangling-bond sites is limited by density of the defects. But at least three structures that can be formed without any seeds other than a "perfect"

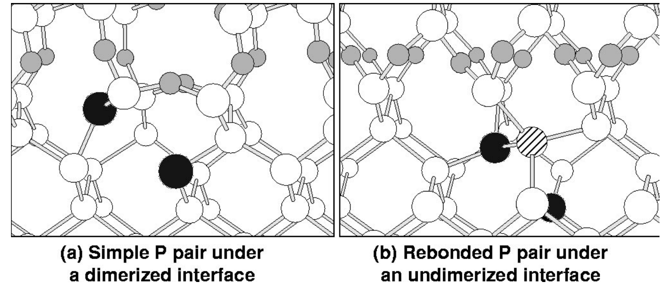


FIG. 7. Phosphorus immobilized in pairs under SiO_2/Si(001) interfaces. (a) P_2^* with an off-center distortion of EL2 type. (b) A rebonded P pair.

SiO_2/Si(001) boundary make it possible to cover the interface with nearly a monolayer of P (or As). These structures involve formation of donor pairs under the interface. The trapped atoms are threefold-coordinated and electrically neutral. The energy gained in these transformations depends on the Fermi energy. This is because the transformation involves a transport of two electrons from Fermi reservoir to the dangling-bond (lone pair) states of two threefold-coordinated P atoms of the pair. Therefore, $E_S^{\mathrm{pair}}=E_S^{\mathrm{pair}}|_{E_\mathrm{F}=0}-2E_\mathrm{F}$; the energy gain is larger in n-type material than in p-type material. Note that the pairing energy is defined as the energy gained per *two* donor atoms: $2\mathrm{P}_{\mathrm{Si}}\rightarrow\mathrm{P}_2+E_S^{\mathrm{pair}}$.

The first one of these three structures involves a pair of two nearest-neighbor, substitutional P atoms [P_2, (Ref. 25]. Such a pair transforms under the interface into a pair of threefold-coordinated P atoms: the P-P bond is broken and one of the P atoms moves into the interstitial region [P_2^*, Fig. 7(a)]. This resembles the behavior of certain donors in bulk III–V compounds and alloys.[27] The value of E_S^{pair} depends on donor species, being higher for As than for P by (0.1–0.2) eV. The inaccuracy of the computed absolute values of E_S^{pair} is about 0.4 eV; the differences between the pairing energies obtained for different structures are often more exact, because most of the numerical errors tend to cancel out in this case.

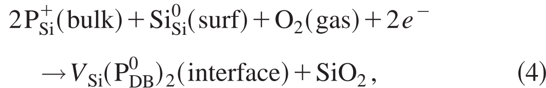
As a result of the transformation of two substitutional, fourfold-coordinated donors into threefold-coordinated, one Si-Si bond is effectively removed. This resembles the case discussed in Sec. III D: without additional energy gain coming from electron localization and from relaxation of stress in the interface, the energy cost of the dissolution of the Si-Si bond would compensate or even overcompensate the energy gain from trapping at dangling-bond sites. Repeating the analysis done in Sec. III D, we obtain (0.2 ± 0.4) eV as the strain energy released due to the formation of the pair under the interface.

It is, therefore, expected that the pairing energy E_S^{pair} depends on the residual stress in the film and on the possibility to relax this stress (i.e., on the oxide and interface structure). Such a dependence is indeed observed. For example, $E_S^{\mathrm{pair}}(E_\mathrm{F}=0.8\ \mathrm{eV})$ of phosphorus is 0.4 eV under the undimerized interface and 0.5 eV under a dimerized interface with oxidized dimers [Fig. 7(a)]. The dimerized interface is favored because the O-Si-P angles become optimal in this

configuration: they can approach the tetrahedral value of 109°. Such optimal angles are not feasible when the interface is undimerized, but even in this case they are closer to tetrahedral than is possible in a P pair embedded in silicon bulk.

In the second structure[24] [Fig. 7(b)], an oxygen interstitial (O_i) and two threefold-coordinated P atoms combine with a {113}-rebonded Si pair. The $113Si_2$ defect is built of two Si atoms that switched bonds with their neighbors,[26] as in cores of {113}-planar agglomerates of Si interstitials.[18,43] The P atoms substitute two nearest-neighbor Si atoms in $113Si_2$, and the P-P bond is broken. The pairing energy is, within numerical accuracy, close to that of P_2^*.

These two pairing mechanisms conserve the number of Si atoms in the substrate. The third pairing mechanism is the reaction



$$2P_{Si}^{+}(\text{bulk})+Si_{Si}^{0}(\text{surf})+O_2(\text{gas})+2e^{-} \rightarrow V_{Si}(P_{DB}^{0})_2(\text{interface})+SiO_2, \quad (4)$$

or trapping of two P atoms by spontaneous ejection of silicon (i.e., by creation of an interface vacancy). The oxide acts here as an efficient sink for the ejected silicon, which is oxidized there by oxygen from the annealing ambient.[46] If the vacancy is created under the interface, its formation energy in the neutral charge state is (2.1 ± 0.4) eV when a free Si surface assumed as the sink for the ejected silicon, that is, when the chemical potential of Si is equal to the chemical potential of a Si atom in bulk silicon.[44] The energy paid for creation of the vacancy is overcompensated by (3.0 ± 0.4) eV gained by segregation of two P atoms to the vacancy site.[47] This yields the pairing energy of $E_s^{\text{pair}}=(0.9\pm0.8)$ eV at $E_F=0.8$ eV.

One might expect even a larger pairing energy when the vacancy is created directly at the interface. In this case, the vacancy formation energy may be as small as 1.2 eV [Fig. 3(d)]. However, such a vacancy is not a good trap for two P atoms, because one of its dimer atoms is oxidized. A better candidate would be the vacancy with a weak dimer bond [Fig. 3(c)], but its formation energy is too high and it turns out that although trapping of two P atoms at such a vacancy releases about 1.8 eV, the pairing energy is only about 0.2 eV. The energy gain is so small also because distortions of atomic bonds around the vacancy are smaller than in a vacancy that is created further away from the interface. This reduced energy gain illustrates the fact that relaxation of these distortions is an important factor in interactions between vacancies and donor atoms.

Nevertheless, it appears that P pairing by silicon ejection from under the interface or from the interface may compete with P pairing by formation of P_2^* and $113Si_2$ defects. The pairing by Si ejection from under the interface seems to be more favorable than the other processes by $\Delta E_s^{\text{pair}}=0.4$ eV. However, ΔE_s^{pair} is inaccurate by about 0.4 eV.[47] Exact calculation of V_{Si} formation energies is generally a difficult task,[17] mostly due to the presence of significant distortions of atomic coordinates even far away from the center of the defect. For this reason we do not emphasize the efficiency of this mechanism. Instead, we prefer a conservative statement that there are several pairing mechanisms possible with the pairing energy of (0.5 ± 0.4) eV.

As a final remark we note that since the ejected Si atoms are oxidized in SiO_2 instead being adsorbed on a free silicon surface, one might expect that the vacancy formation energy should be adjusted by adding to it the difference between the energy of two Si-Si bonds (cohesive energy of Si) and the energy of two Si-O bonds, that is, it should be lowered by ≈ 3 eV. However, such an adjustment would not be correct because, in spite of being covered by SiO_2, the silicon surface still acts as a reservoir of Si atoms. Indeed, interface steps can adsorb and eject Si atoms[44] and the SiO_2 film can easily adapt itself to the changed geometry, for example, by dangling-bond diffusion discussed in Sec. III D. In other words, the role of interface steps is formally the same as the role of steps on free surface.[44] The chemical potential of the Si reservoir then becomes equal to the chemical potential of a Si atom in bulk silicon, because the silicon crystal is an infinitely larger reservoir of atoms than the SiO_2 film. The situation would be different if the film could not adapt its shape to changes in the step shape. In this case, adsorption or emission of Si from steps would be possible only through creation of high-energy defects.

IV. SEGREGATION MODEL

In this section we will compare the results of this analysis with experimental data on the dependence of the interfacial segregation constant on phosphorus concentration and on the annealing temperature.

Pairing of dopants affects the functional form of the dependence of the density D_P of the segregated P on the concentration C_P of active P in bulk close to the interface. In order to estimate the magnitude of this effect, we assume that P can be bonded at the interface by pairing and/or trapping, that the corresponding reaction constants are thermally activated with energies E_p and E_t, and that P atoms are in local equilibrium.[21] Consider N_{deact} deactivation sites existing under the interface. The deactivation rate r is proportional to the density $N_f=N_d-D_P$ of free deactivation sites, while the activation rate $\bar{r}$ is proportional to the density D_P of the occupied sites

$$r\sim(N_{\text{deact}}-D_P) \quad (5)$$

$$\bar{r}\sim D_P. \quad (6)$$

The important difference between the deactivation rates for trapping and pairing is that the former is proportional to C_P, while the latter is proportional to C_P^2.

In thermodynamical equilibrium we have $r=\bar{r}$, leading to

$$D_P=\frac{N_p C_P^2}{C_P^2+B_p^2\exp(-E_p/kT)} \quad (7)$$

when segregation is dominated by pairing ($N_{\text{deact}}=N_p$), and to

$$D_P=\frac{N_b C_P}{C_P+B_t\exp(-E_t/kT)} \quad (8)$$

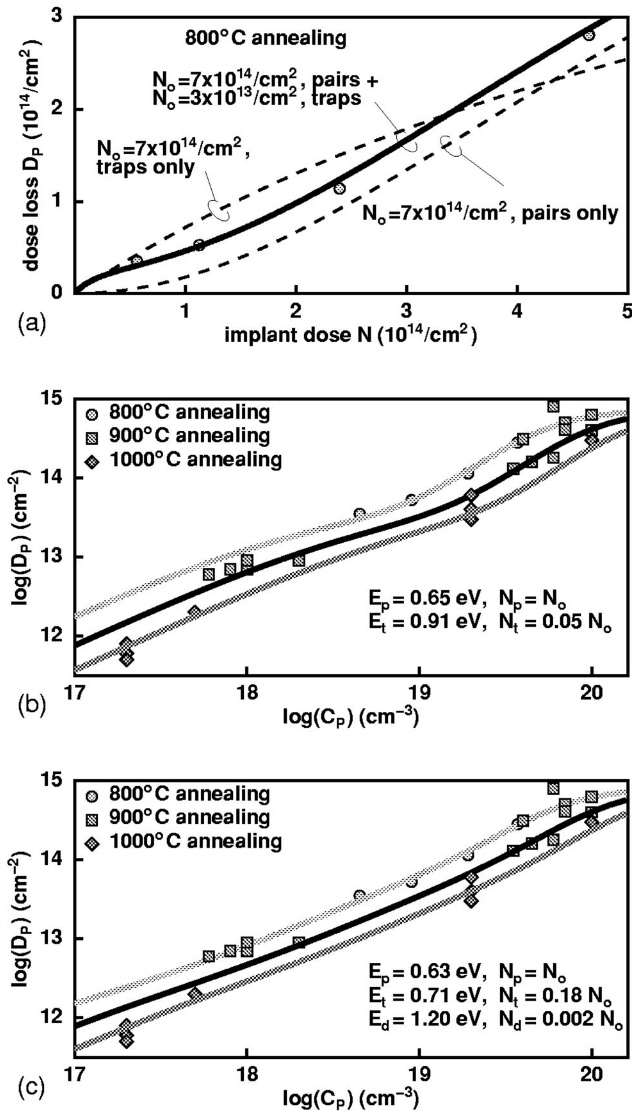


FIG. 8. Phosphorus dose loss, D_{P}. (a) Dependence of D_{P} on implant dose N, SIMS data from Refs. 7 and 48. One pairing and one trapping mechanism assumed. (b) Dependence of D_{P} on P concentration C_{P} close to the interface, SIMS data after annealing at 800 °C,[7,48] 900 °C,[21,11] and 1000 °C.[42] Fit with the same parameters as in the upper panel. (c) The same dependence as in the mid panel but fitted with E_t well within the error bar of the *ab initio* estimate. Trapping on $N_d = 10^{12}/\mathrm{cm}^2$ dangling bonds was added for completeness.

when trapping dominates ($N_{\mathrm{deact}} = N_b$). B_p^2 and B_t are proportional to the reaction constants for pairing and trapping. For simplicity, we have neglected the small amount of P dissolved in the volume of SiO_2.[21] We have also assumed that $N_p = N_o = 1$ ML, that is, all geometrically possible pairing sites can be occupied.

The resulting functional dependence (Fig. 8) compares favorably with the published data.[7,21,11,42] (The areal concentration of lost dopants D_{P} can be obtained by comparison of SIMS profiles obtained first after implantation through an oxide film with those obtained by annealing, and finally with those obtained by stripping the oxide.) Numerical fit to these data yields $E_p = (0.7 \pm 0.3)$ eV and $E_t = (0.9 \pm 0.2)$ eV.[49,50] In order to reduce the number of parameters, we set $B_p = B_t = N_o$, that is, we ignored entropy contributions other than those due to the number of lattice sites.[51] For simplicity, we also assumed that the contributions from all mechanisms are additive; indeed, two different mechanisms compete only in a narrow range of C_{P}.

The fitted energies are compatible with our *ab initio* estimates for P pairing ($E_p = 0.5 \pm 0.4$ eV at $E_{\mathrm{F}} = 0.8$ eV, Sec. III E), for trapping at dangling-bond sites ($E_{o0n3} = 1.1 \pm 0.2$ eV, Sec. III C), and for trapping at defects with unoxidized Si atoms ($E_{o0n4} = 0.5 \pm 0.3$ eV at $E_{\mathrm{F}} = 0.8$ eV, Sec. III D). Figure 8(c) shows a fit with a trapping energy closer to the *ab initio* estimate, with the contribution from trapping at dangling-bond sites included.

The fitted value of N_b for trapping is as high as 0.05–0.15 ML, many times higher than the typical density N_d of electrically active interfacial defects created during thermal oxidation ($N_d \simeq 0.002$ ML). In other words, there exists a regime of segregated P concentration between roughly $10^{12}/\mathrm{cm}^2$ and $10^{13}/\mathrm{cm}^2$ in which the segregation can be explained neither by trapping at electrically active defects nor by pairing. In this regime, the only plausible candidates for donor traps we have identified are defects with unoxidized interfacial silicon atoms, such as in partially unoxidized step ledges and in Si-Si bridges connected with the substrate by unoxidized backbonds (Sec. III D). The areal density of the ledge atoms can be estimated from the areal density of atoms on Si(001) step edges. Assuming one unoxidized Si atom per step unit length and taking steps of monatomic height, we obtain 0.05 ML of traps for 1° average deviation of the surface normal from the (001) direction. Note that the roughening of the interface in the course of thermal oxidation may possibly lead to formation of sites resembling atomic steps. Silicon bridges also constitute a significant percentage of bonds in the oxide layer close to the boundary with the silicon (so-called SiO_x interface layer). It is, therefore, plausible that a realistic SiO_2/Si(001) interface has even as much as ~ 0.2 ML unoxidized interfacial Si atoms that may act as P traps.

V. SUMMARY AND CONCLUSIONS

In summary, we have presented an *ab initio* study of P and As segregation to SiO_2/Si(001) interfaces. A simple, physically based model of segregation was formulated. The coexistence of pairing and single-atom trapping causes a two-regime dependence of the segregation coefficient on the implant dose.

Trapping of single donor atoms is possible at unoxidized dangling-bond sites (electrically ative defects) and at unoxidized, fourfold-coordinated Si atoms in defects at the interface (electrically inactive defects) such as unoxidized step ledges, and silicon bridges attached directly to the substrate. In the case of trapping at electrically active defects, the energy gain is high but the process is efficient only for very low dopant concentrations. In the case of trapping at electrically inactive defects, the energy gain is lower but the process is efficient also at high dopant concentrations. The latter mechanism relies on migration and recombination of Si dan-

gling bonds and on reoxidation of the resulting silicon bridges. Therefore, we expect that it can be largely suppressed by any treatment that significantly reduces mobility of Si dangling bonds, and by reduction of oxygen content in the annealing ambient. We found that mobility of dangling bonds is associated with low energy of local deformations of SiO_2 network, caused by the presence of Si-O-Si "boomerangs" that can easily rotate and change their internal angles. The conclusion from this observation is that the mobility should be diminished, for example, by nitridation of the interface layer, because in this case numerous flexible OSi_2 "boomerangs" are substituted by rigid NSi_3 "anchors."[52]

At very high dopant concentrations, dopant pairing mechanisms dominate. They allow the interface to be covered with up to a monolayer of immobilized and deactivated donors. This pairing occurs under the interface and is not associated with any seed defects. It can be realized either through local reorganization of atoms (either a bond breaking in a nearest-neighbor pair of substitutional donors followed by an off-center displacement of one of the donor atoms, or a rebonding similar to that found in {113}-planar defects followed by breaking of the donor-donor bond), or through ejection of a lattice Si atom to the oxide (i.e., through spontaneous formation of a Si vacancy).

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[45] We define the energy of a Si-Si bond in the crystal as a half of silicon cohesive energy. The quoted energy of 2.6 eV is a theoretical LDA value. The experimental bond strength is by $\sim$0.3 eV lower than computed by LDA. Such a moderate overbinding is a typical LDA effect, compatible with LDA bond lengths being routinely computed slightly shorter than found in experiment.

[46] Annealing is usually done in an ''inert'' N_2 ambient. However, this ''inert'' N_2 atmosphere contains some oxygen. Annealing in a strictly nonoxidizing environment is destructive to the oxide: the SiO_2 film loses oxygen to the ambient by emission of SiO.

[47] The numerical uncertainty is larger here than in calculations for the other pairing mechanisms due to an additional inaccuracy that comes from the calculation of the binding energy of V_{Si} under the interface. A vacancy is surrounded by a long-range strain field, which is not properly accounted for in our calculations. This problem is less severe when the vacancy sits directly at the interface, because in this case the atoms around the vacancy can relax in such a way that most of the distortions are in the soft SiO_2 film.

[48] We assume that the number of P atoms diffused to the interface is proportional to the implant dose.

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