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Proton-Induced Fixed Positive Charge at the Si(100)-SiO$_2$ Interface

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Positively charged defects induced by protons at the Si(100)-SiO$_2$ interface are studied through density-functional calculations and realistic interface models. Protons generally preserve the bonding network, but cause the spontaneous breaking of strained bonds leading to threefold-coordinated Si(3)$^+$ and O(3)$^+$. Defect energies fall within a band of ~ 0.5 eV, which is stabilized by ~ 0.3 eV at the interface. Only the O(3)$^+$ at ~ 1 eV lower energies stand out as deep defects. This description is consistent with several experimental observations and supports the O(3)$^+$ as the origin of the fixed positive charge generated during silicon oxidation, in accord with a previous suggestion inferred from electrical data.

Current metal-oxide-semiconductor electronic devices are approaching dimensions in which the control of interface defects is critical for device performance. Hydrogen-related defects are particularly important given the ubiquitous nature of this species. A H$_2$ anneal is generally necessary to passivate defects like P_b centers and meet operating requirements [1]. However, hydrogen is also known to induce positive charging [2–6] and may affect the reliability of the electronic device [7]. Isotopic substitution experiments clearly revealed an intimate link between positive charging and mobile protons [5]. Electron-spin resonance (ESR) measurements indicated that the charge is diamagnetic [4]. The generated charge state is naturally attributed to hydrogen bonding to a bridging oxygen in analogy with the formation of the hydronium ion in water [2,4], but also the bond centers of Si-Si bonds have been advanced as possible defect sites in more defective structures [3]. Moreover, hydrogen has also been proposed to induce bond-breaking processes leading to the formation of more general Si$_{3-n}$H$_n$O$^+$ overcoordinated O centers [6] or of ESR-active E'_1 centers [8]. Proton-induced overcoordinated oxygen centers, formed either with [6] or without [4] bond-breaking processes, have been suggested as the origin of the fixed positive charge observed upon silicon oxidation [9]. A further distinction between hydrogen-induced positively charged states could be established experimentally through the observation of mobile and immobile species [10]. From the theoretical side, proton equilibrium sites have been determined at bridging O atoms and at O vacancies [11]. However, the rich body of experimental evidence suggests that the role of protons at the Si-SiO$_2$ interface is more complex and calls for a broader description of the underlying physics.

In this work, we investigate proton-induced processes at the Si(100)-SiO$_2$ interface giving rise to positive charging using an interface model structure which realistically describes the transition between crystalline silicon and amorphous SiO$_2$ [12,13]. Our study yields a comprehensive description including four different forms of proton-induced positively charged states. A clear distinction is

provided between shallow and deep proton equilibrium sites and linked to the experimental observation of mobile and immobile species [10]. Bridging O atoms and O vacancies, which both count among the shallow sites, are found to give equilibrium sites of comparable energy and to show an enhanced stability in the interfacial region. In the case of strained Si-O or Si-Si bonds, these equilibrium configurations can spontaneously evolve through bond rearrangements to deeper defect states, such as positively charged threefold-coordinated Si(3)$^+$ or O(3)$^+$. In particular, O(3)$^+$ states are found to be deeper than other charge forms by ~ 1 eV and show electrical characteristics in accord with those of the fixed positive charge at the Si-SiO$_2$ interface observed upon silicon oxidation [9]. Therefore, our description supports the interpretation inferred from electrical measurements that the origin of this charge results from proton-induced bond-breaking processes leading to overcoordinated oxygen centers [6].

For the Si(100)-SiO$_2$ interface, we used a superlattice structure containing 217 atoms, in which crystalline Si (9 monolayers) and amorphous SiO$_2$ (~ 17 Å) alternate [12,14]. The substoichiometric oxide at the interface extends over a thickness of ~ 6 Å and shows a distribution of intermediate oxidation states of Si in accord with photoemission data [13]. The simulation cell in the transverse directions corresponds to a $\sqrt{8} \times \sqrt{8}$ Si(100) interface unit. The electronic structure was described within a generalized gradient approximation to density-functional theory [15,16]. Structural relaxations were carried out through damped *ab initio* molecular dynamics [19].

Density-functional calculations have found that hydrogen gives $+/-$ charge transition levels in the band gap for both Si [20] and SiO$_2$ [21,22]. Considering the band alignment at the Si-SiO$_2$ interface [23], we infer that protons are stable in both interface components for Fermi energies in the lower part of the Si band gap. This assertion is also supported by general considerations [24].

We here address the positive charge state of hydrogen in sites located on both sides of the interface. Considered

defect sites correspond to protons located in Si-Si bonds and attached to bridging O atoms, as illustrated in Figs. 1(a) and 1(d). Both defect sites also occur in the suboxide region. To compare the relative defect energetics, we inserted the proton in both kinds of sites across the interface, and carried out full structural relaxations. Our statistics comprises 70 distinct sites.

For all the considered defects, we give in Fig. 2 their formation energy [22] vs their position with respect to the interface. We here referred the H energy to half the energy of the H_2 in an interstitial void of amorphous SiO_2 and took the Fermi level at the top of the Si valence band. First, we discuss the defect states which do not give rise to bond rearrangements. Deep into the oxide, the average formation energy of a proton bonded to a bridging O atom is about 0.75 eV, with a spread of 0.19 eV. This spread is typical for amorphous SiO_2 and results from the structural disorder [25].

On the Si side of the interface, i.e., in the channel, we found that all Si-Si bond centers can accomodate protons in locally stable configurations, in accord with previous calculations for bulk Si [20]. Their formation energy (0.79 eV) is found to be comparable to those of protons attached to bridging O atoms on the oxide side of the interface. Bond centers in the channel are transited by mobile protons until these interact with negatively charged acceptors forming a neutral complex [26]. A modest thermal treatment is sufficient to eliminate these mobile protons and recover the intended electrical activity.

In the interfacial region, we observe for both kinds of defect a minor stabilization (∼0.2–0.4 eV), which results from the enhanced dielectric screening due to image-charge effects and from the higher structural relaxation energies due to the more flexible bonding network. The proton stabilization which emerges from our calculations is fully consistent with available experimental evidence. Using nuclear reaction analysis, Krauser *et al.* showed that there is a peak for the H distribution at the Si-SiO$_2$ interface [27]. Upon annealing of such interfaces in hydrogen, the analysis of internal photoemission experiments also indicates that the positive charge is located in the very first oxide layers at the interface [4,8].

For some of the investigated sites close to the interface, the network structure spontaneously underwent a bond-breaking process, which gave rise to a positively charged threefold-coordinated Si atom [Si(3)$^+$]:

$$Si\text{-}H^+\text{-}Si \rightarrow Si(3)^+ + Si\text{-}H, \tag{1}$$

$$Si\text{-}OH^+\text{-}Si \rightarrow Si(3)^+ + Si\text{-}O\text{-}H, \tag{2}$$

as illustrated in Figs. 1(b) and 1(e), respectively. The energies of these defects fall on the low edge of the band corresponding to the non-bond-breaking defects (at energies of ∼0.1 eV).

To understand the origin of the bond-breaking processes, we investigated the relation between bond lengths and defect stability. For each considered Si-Si bond, we display in Fig. 3(a) the defect formation energy vs its bond length prior to proton insertion. We observe a rather constant defect energy for bond lengths up to 2.38 Å, which correspond to non-bond-breaking defects states with the proton located at the bond center. For larger Si-Si bond lengths, the insertion of the proton causes bond rupture yielding defect states of significantly lower energy. Similarly, we

FIG. 1 (color online). Atomic representation of typical H$^+$-related defects at the Si-SiO$_2$ interface: Si-H$^+$-Si (left column) and Si-OH$^+$-Si (right column) and their evolution to atomic structures involving threefold-coordinated Si [Si(3)$^+$, second row] and O [O(3)$^+$, third row] atoms.

FIG. 2. Formation energy of H$^+$-induced defects vs position with respect to the Si(100)-SiO$_2$ interface. The shaded area encloses typical energies of defects which do not involve bond breaking (closed symbols): Si-H$^+$-Si (squares) and Si-OH$^+$-Si (circles). Open symbols refer to defects involving bond breaking, giving Si(3)$^+$ [with either Si-H (squares) or Si-O-H (circles) bonds] and O(3)$^+$ defects (diamonds). The lower case letters in the legend refer to panels in Fig. 1.

FIG. 3. Defect formation energy vs (a) Si-Si bond length prior to H^+ insertion at the bond center and (b) Si-O bond length prior to H^+ attachment to the bridging O atom. The lines correspond to linear regressions of the formation energies of non-bond-breaking defects (closed symbols). The notation is the same as in Fig. 2.

give in Fig. 3(b) the formation energy of Si-OH$^+$-Si defects vs the average of the two involved Si-O bonds prior to proton attachment. A clear decreasing trend is recognizable despite the scatter. For strained Si-O bonds, this behavior is understood by recalling that the attachment of a proton to a bridging O atom causes an elongation of the Si-O bond length [22], whereby the strain in the bond can be relaxed. Proton-induced bond breaking leading to Si(3)$^+$ defects is only observed for elongated Si-O bonds (longer than 1.7 Å). Since such bonds primarily locate in the suboxide region [12,28], bond-breaking events will more likely occur close to the interface. The appearance of the resulting undercoordinated Si defects is consistent with the increase in the concentration of paramagnetic P_b and E' centers observed upon postoxidation annealing in H_2 [8,29].

On a few occasions, upon a proton-induced Si-Si bond breaking, the structure evolved further, bringing the Si(3)$^+$ to form a bond with a nearby O atom [Fig. 1(c)]. This gave rise to the formation of a positively charged threefold-coordinated O atom [O(3)$^+$], similar to the puckering configuration of the E' center [30]. This evolution corresponds to a lowering of the energy by ~1 eV, resulting in much deeper defect states. The formation of O(3)$^+$ only occurred in the top layer of the substrate, where our model shows a noncrystalline pattern of Si-Si bonds [12,13,31]. We did not observe O(3)$^+$ formation following a Si-O bond-breaking process.

Several observations are consistent with the occurrence of O(3)$^+$ defects. Warren *et al.* found that H-induced positive charging in Si-SiO$_2$ structures is very different from simple oxygen vacancy hole traps, and invoked the formation of overcoordinated O centers involving either H

or Si neighbors (Si$_{3-n}$H$_n$O$^+$ centers) to explain their observations [6]. Interestingly, these authors also found that the H-induced positive charging is largely enhanced in Si-rich oxide structures, in accord with our finding O(3)$^+$ close to the silicon substrate.

Proton-induced O(3)$^+$ defects might also play a key role during silicon oxidation. Ubiquitous protons would generate such defect units providing a mechanism by which the amorphization of the oxide network is facilitated [31]. Furthermore, the occurrence of these defects is consistent with the fixed positive charge, which is found near the interface upon thermal oxidation of silicon [9]. Electrical measurements indicate that these positive defects can induce negative charge in the silicon substrate [9] and that their neutralization levels lie outside of the Si band gap [32]. To verify this behavior for the O(3)$^+$ defects, we investigated the O(3)$^+$ state for varying Fermi level across the Si band gap. Figure 4(a) illustrates the thermodynamically most stable levels of the O(3)$^+$ defect for this evolution. This defect is found to be always lower than the other proton-induced defects identified in this work, supporting the stable nature of the O(3)$^+$ [9,32]. Our calculations [33] show that upon charging the additional electron goes to the Si conduction band (Fig. 4). The positive O(3)$^+$ attracts the extra electron, leading to a localization of its center of charge at a distance of ~5 Å from the interface [Fig. 4(b)]. These properties are consistent with the electrical features of the fixed positive charge at the Si-SiO$_2$ interface, supporting its assignment to the O(3)$^+$.

Our study also provides an understanding for the observation of mobile and static hydrogen-related species at Si-SiO$_2$ interfaces [10]. We distinguish mobile and static positive charge on the basis of the 1 eV-energy difference

FIG. 4. (a) Defect formation energy vs Fermi level in the Si band gap for the lowest-energy proton-induced defects of each kind found in Fig. 2. (b) Charge density distribution of an extra electron at the interface in the presence of an O(3)$^+$. The positions of the center of charge of the extra electron and of the O(3)$^+$ are indicated by arrows.

separating the $O(3)^+$ defect levels from the other defect levels. Our calculated defect energies support the assignment of mobile positive charge to Si-OH$^+$-Si [10], but also to Si-H$^+$-Si and Si(3)$^+$. Indeed, proton diffusion in the oxide can be well described as hopping between Si-O-Si units [25]. However, in the vicinity of the interface, Si-H$^+$-Si and Si(3)$^+$ defects occur at comparable energies and may also be transited by mobile protons. The static positive charge is assigned to deep $O(3)^+$ defects which are assumed to be immobile [10,32], because of the important structural relaxation that these defects involve.

In agreement with experiment [35], our results imply that the concentration of available sites for the fixed charge is much lower than for the mobile charge. Almost any Si-Si bond or bridging O atom can serve as an equilibrium site for mobile protons, but $O(3)^+$ can only arise in the presence of elongated bonds. Both fixed and mobile protons contribute to the positive charge. However, because of their deep energy, the $O(3)^+$ sites are preferred and will remain occupied even at elevated temperatures when the mobile protons are swept away.

From our investigation of proton-induced positive charge at the Si-SiO$_2$ interface, a picture emerges in which a variety of different defects occur. In particular, we address their location with respect to the interface, their respective energy levels, and the role of strained bonds. Our description provides a comprehensive interpretation of a series of experimental observations.

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[1] K. L. Brower, Phys. Rev. B **38**, 9657 (1988).

[2] J. M. M. de Nijs et al., Appl. Phys. Lett. **65**, 2428 (1994).

[3] K. Vanheusden and A. Stesmans, Appl. Phys. Lett. **64**, 2575 (1994).

[4] V. V. Afanas'ev and A. Stesmans, Appl. Phys. Lett. **72**, 79 (1998); Phys. Rev. Lett. **80**, 5176 (1998).

[5] V. V. Afanas'ev and A. Stesmans, Europhys. Lett. **53**, 233 (2001).

[6] W. L. Warren et al., Appl. Phys. Lett. **68**, 2993 (1996).

[7] D. J. DiMaria, D. Arnold, and E. Cartier, Appl. Phys. Lett. **61**, 2329 (1992).

[8] V. V. Afanas'ev and A. Stesmans, Mater. Sci. Eng. B **58**, 56 (1999).

[9] B. E. Deal et al., J. Electrochem. Soc. **114**, 266 (1967); B. E. Deal, ibid. **121**, 198C (1974).

[10] K. Vanheusden, W. L. Warren, and R. A. B. Devine, J. Non-Cryst. Solids **216**, 116 (1997).

[11] S. N. Rashkeev et al., Appl. Phys. Lett. **81**, 1839 (2002).

[12] F. Giustino and A. Pasquarello, Phys. Rev. Lett. **95**, 187402 (2005).

[13] A. Bongiorno et al., Phys. Rev. Lett. **90**, 186101 (2003); A. Bongiorno and A. Pasquarello, Appl. Phys. Lett. **83**, 1417 (2003).

[14] For a single Si-SiO$_2$ interface, the formation energy of a singly charged defect located deep into the substrate (oxide) can be obtained from our supperlattice results by a correction of $+0.043$ eV (-0.122 eV).

[15] J. P. Perdew et al., Phys. Rev. B **46**, 6671 (1992).

[16] We used a norm conserving pseudopotential for Si [17] and ultrasoft pseudopotentials for H and O [18]. The electron wave functions and charge density were described by plane wave basis sets with cutoffs of 24 and 150 Ry, respectively [19]. The Brillouin zone was sampled at the Γ point. A uniform background charge was used to compensate the defect charge. Associated energy corrections vary with position of the charged defect. We estimate corrections of 0.05 and 0.17 eV for positively charged defects located deep into the Si and SiO$_2$ layers, respectively.

[17] A. Dal Corso et al., Phys. Rev. B **53**, 1180 (1996).

[18] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[19] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985); A. Pasquarello et al., Phys. Rev. Lett. **69**, 1982 (1992); K. Laasonen et al., Phys. Rev. B **47**, 10 142 (1993); we used the implementation in the QUANTUM-ESPRESSO package, http://www.democritos.it.

[20] C. G. Van de Walle et al., Phys. Rev. B **39**, 10 791 (1989).

[21] S. T. Pantelides et al., IEEE Trans. Nucl. Sci. **47**, 2262 (2000).

[22] J. Godet and A. Pasquarello, Microelectron. Eng. **80**, 288 (2005).

[23] F. Giustino, A. Bongiorno, and A. Pasquarello, Appl. Phys. Lett. **86**, 192901 (2005); J. Phys. Condens. Matter **17**, S2065 (2005).

[24] C. G. Van de Walle and J. Neugebauer, Nature (London) **423**, 626 (2003).

[25] J. Godet and A. Pasquarello, Phys. Rev. Lett. **97**, 155901 (2006).

[26] C. G. Van de Walle and B. R. Tuttle, IEEE Trans. Electron Devices **47**, 1779 (2000); in n-type Si, H$^-$ is the stable H form and forms a neutral complex with a donor.

[27] J. Krauser et al., Microelectron. Eng. **22**, 65 (1993).

[28] A. Bongiorno and A. Pasquarello, Phys. Rev. B **62**, R16 326 (2000).

[29] A. Stesmans and V. V. Afanas'ev, Appl. Phys. Lett. **72**, 2271 (1998).

[30] J. K. Rudra and W. B. Fowler, Phys. Rev. B **35**, 8223 (1987); M. Boero et al., Phys. Rev. Lett. **78**, 887 (1997).

[31] A. Pasquarello, M. S. Hybertsen, and R. Car, Nature (London) **396**, 58 (1998).

[32] D. S. Ang and S. Wang, IEEE Electron Device Lett. **27**, 914 (2006).

[33] Density-functional calculations are generally accurate for total energy differences, whereas the alignment of defect levels with respect to band edges is preferably based on a comparison with experiment. For the Si dangling bond, the present alignment gives charge transition levels at $E_{+/0} = 0.32$ eV and $E_{0/-} = 0.66$ eV with respect to the top of the Si valence band (cf. Fig. 4), in good agreement with capacitance-voltage measurements which identify these levels at 0.26 and 0.84 eV [34].

[34] E. H. Poindexter et al., J. Appl. Phys. **56**, 2844 (1984).

[35] P. J. Macfarlane and R. E. Stahlbush, Appl. Phys. Lett. **77**, 3081 (2000).