

First-principles analysis of hole-induced Si—H bond dissociation in silicon dioxide

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Silicon dioxide (SiO₂) is arguably one of the most technologically relevant materials due to its use as a native gate dielectric in silicon-based metal-oxide-semiconductor transistors. In such devices, hydrogen is intentionally introduced during a forming gas anneal to passivate electrically active defects, which would otherwise degrade device performance. While the Si—H bonds resulting from this passivation process are highly stable and mostly chemically inert, it has been deduced from experiments and first-principles calculations that radiation-induced holes in the SiO₂ valence band mediate the release of H⁺ from such bonds in the oxide. Here, we show through first-principles calculations combined with the theory of multiphonon emission that isolated Si—H bonds in SiO₂ can be easily broken upon capturing a hole. Our calculations show that capturing holes from the SiO₂ valence band leads to an efficient Si—H bond dissociation mechanism, with a large effective capture cross section of $\sigma = 6 \times 10^{-15} \text{ cm}^2$. The resulting H⁺ can easily diffuse away, leaving behind a neutral paramagnetic E' center, i.e., an O₃ = Si· dangling bond, confirming earlier results reporting H⁺ release and E' center creation upon hole injection into the SiO₂ valence band.

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I. INTRODUCTION

Metal-oxide-semiconductor (MOS) transistors based on silicon are the fundamental building blocks of most electronic devices. Although many other semiconductors have superior electrical characteristics such as higher carrier mobilities [1] or larger bandgaps [2], silicon is still the most widely used semiconductor due to its ability to form high-quality interfaces with its native oxide SiO₂. This allows for a simple and robust process to grow a gate dielectric on top of the device channel. While SiO₂ exhibits a lower defect concentration compared to other common gate dielectrics like HfO₂ [3], optimal device performance still requires hydrogen passivation of remaining Si dangling bonds (DB) and other defects at the interface and within the oxide, [4] which is accomplished during a forming gas anneal. In this process step, Si-DBs, which would otherwise act as charge trapping [5] or

recombination centers, are converted to highly stable and electrically inactive Si—H bonds.

Since the Si—H bond has a large binding energy of 2.5 eV [6] and 4.2 eV [7] relative to an interstitial H⁰ in Si and SiO₂, respectively, purely thermal bond dissociation is highly unlikely under normal conditions. Here, we therefore focus on dissociation triggered by the presence of carriers.

While the electronic states of Si—H bonds in Si or at the Si/SiO₂ interface are in resonance with the Si valence band (VB) [8], Si—H bonds in the SiO₂ dielectric possess a doubly occupied state slightly above the SiO₂ valence-band maximum (VBM) as shown in the band diagram in Fig. 1, with band offsets [9] and the SiO₂ bandgap [10] taken from the experimental literature. Since this state is in the bandgap of the oxide, the Si—H bond in principle can capture a hole from the SiO₂ VBM. Hence, even capturing a single carrier has a reasonable chance to cause a dissociation of the Si—H bond. This process is thus relevant for understanding irradiation damage within the gate dielectric, as it was deduced from experiments in the 1970s that holes in the SiO₂ VB created by ionizing radiation, e.g., x-rays, are likely responsible for the release of H⁺ from hydrogenated defects in the oxide [11]. Indeed, Afanas'ev and Stesmans later demonstrated experimentally that hole injection into the SiO₂ VB leads to the

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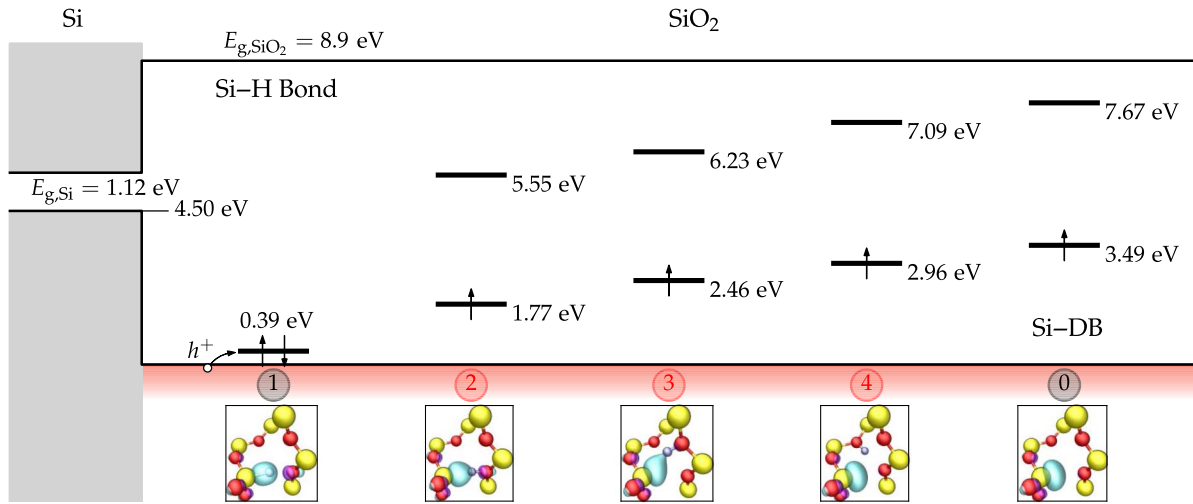


FIG. 1. Band diagram of a Si/SiO₂ interface with the single-particle Kohn-Sham energies of a Si—H bond (state 1) along its dissociation path toward an isolated Si dangling bond (state 0) as obtained from our calculations. An isolated Si—H bond (1) introduces a bonding state approximately 0.39 eV above the VBM of SiO₂. Due to the large energetic distance to the Si VBM, this state can only trap holes from the SiO₂ VB.

creation of E' centers, i.e., dangling bonds at a threefold oxygen-coordinated Si atom ($O_3 = Si\cdot$), which is also correlated with the release of H^+ [12]. These findings strongly suggest that Si—H bonds dissociate upon hole trapping from the SiO₂ VB. In their experimental work [12], Afanas'ev and Stesmans determined this H^+ release mechanism to have a large effective hole capture cross section (CCS) of $\sigma = 3 \times 10^{-14} \text{ cm}^2$.

Due to its technological relevance, the Si—H dissociation mechanism in SiO₂ also has been extensively studied theoretically using density functional theory (DFT). In particular, Pantelides and collaborators employed such calculations to deduce a mechanism by which holes at the top of the oxide VB mediate the release of H^+ from hydrogenated defects in SiO₂ [13] (as proposed in Ref. [11] rather than as neutral H, leaving the defect positively charged, as proposed later in Ref. [14]). They further demonstrated that H^+ arriving at the Si/SiO₂ interface leads to depassivation of DBs via direct H₂ formation [15] and can be used to account for several other observed radiation-induced phenomena [16,17]. Other early work on crystalline α -quartz also showed that Si—H bonds within a H-decorated oxygen vacancy, a so-called hydrogen bridge [18], can dissociate with a thermal barrier of 1.15–1.30 eV after capturing a hole [19,20]. The resulting H^+ then attaches itself to a nearby bridging O atom of the SiO₂ network from which it can further diffuse away via a ring-crossing mechanism with a predicted barrier of 0.5 eV [21,22], in good agreement with the experimental H^+ diffusion barrier of 0.38 eV [23]. Later studies used more accurate hybrid functionals and also investigated the dissociation of isolated Si—H bonds in amorphous SiO₂ (a-SiO₂) [22]. It was shown that

the dissociation process upon hole capture can happen spontaneously but can also be associated with a small thermal barrier in the range of 0.1–0.5 eV depending on the local chemical environment.

All these theoretical studies of hole-induced H^+ release from Si—H bonds in SiO₂ are based on ground-state total-energy calculations for different configurations. As suggested by Fig. 1, in a ground-state DFT calculation an injected hole always ends up being trapped at the previously doubly occupied Si—H state within the SiO₂ bandgap. However, in this treatment the actual hole trapping process from the SiO₂ VB is neglected under the assumption that the subsequent dissociation and diffusion of H^+ is the rate-limiting step. To the best of our knowledge, this critical assumption has not been investigated in the literature yet.

In this work, we close this gap by using a hybrid functional DFT approach combined with the theoretical framework of nonradiative capture via multiphonon emission (MPE) [24] to study the hole capture process directly. We show for a prototypical isolated Si—H bond in α -quartz that the hole trapping (from state 1 to 2 in Fig. 1) indeed happens very fast, with a predicted hole capture cross section of $\sigma = 6 \times 10^{-15} \text{ cm}^2$, in good agreement with the experimental values obtained by Afanas'ev and Stesmans [12]. Our calculations also indicate that this efficient trapping mechanism is caused by the pronounced anharmonicity of the Si—H bond dissociation and is thus *not* self-evident simply from the Kohn-Sham energies presented in Fig. 1. Within the MPE framework, this anharmonicity reduces the classical capture barrier from 0.99 eV in the harmonic approximation to only 23 meV. Hole capture is therefore nearly temperature independent and is

not the rate-limiting step of the experimentally observed hole-induced H^+ release. This kinetic information is not accessible from previous works [22,25], which only studied the energetics *after* hole trapping. We further show that the resulting H^+ only needs to overcome a barrier of 0.72 eV to leave the vicinity of the formed Si-DB (states 2–4 in Fig. 1) and thus can be considered to be mobile, eventually leading to an isolated Si-DB (state 0).

The remainder of this paper is organized as follows. In Sec. II, we describe the hybrid-functional DFT framework used to compute the electronic structure and formation energies of Si–H bonds in SiO_2 , the construction of the atomistic model used to represent the Si–H bond, and the MPE formalism employed to obtain the hole capture rate. In Sec. III, we present our main results, beginning with the basic electronic structure of the Si–H bond, then analyzing the hole-induced dissociation mechanism and finally discussing the subsequent migration of the released H^+ away from the defect site. We also show that the Si–DB/ H^+ complex in crystalline α -quartz behaves in a similar way as in a- SiO_2 . Section IV summarizes the key findings and their implications for irradiation-induced degradation and the reliability of Si/ SiO_2 -based MOS devices.

II. COMPUTATIONAL METHODS

A. DFT framework

We employ hybrid-functional DFT as implemented in the CP2K [26] code. The Gaussian plane wave approach [27] is used to combine the advantages of Gaussian atomic basis sets and plane waves for representing wavefunctions and electron densities. All calculations were performed with the separable Goedecker-Teter-Hutter pseudopotentials and the corresponding double- ζ atomic basis sets including polarization functions [28]. The kinetic energy cutoff for the auxiliary plane-wave basis was set to 1000 Ry. In order to obtain an accurate electronic structure, in particular for localized states, we use the HSE screened hybrid functional [29]. Here, the auxiliary density matrix method [30] is utilized together with the pFIT3 auxiliary basis set to mitigate the large computational costs associated with the calculation of exact exchange. All calculations in this work are spin-polarized to allow for open shells as is required to describe a Si dangling bond. The total energy of the system was self-consistently converged down to a threshold of 2.7×10^{-6} eV. Cell and geometry relaxations were performed with a convergence threshold of 0.01 GPa for stress and 5 meV $\text{\AA}^{-1}$ for atomic forces. Thermal barriers and reaction pathways of the H^+ migration are determined using the well-established climbing image nudged elastic band method (CI-NEB) [31] with a spring force constant of 2.5 eV $\text{\AA}^{-1}$. In order to accelerate the CI-NEB calculation, we use a geodesic estimator [32] to construct an improved initial guess for the reaction paths.

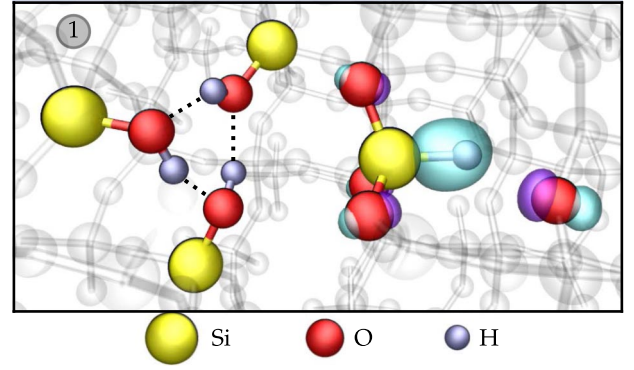


FIG. 2. Atomic structure after removal of a Si–O unit followed by passivation of all dangling bonds with H. The OH groups form a ring due to mutual H bonding, whereas the puckered Si–H bond is isolated and only weakly interacts with an O nearby, as indicated by the plotted isosurfaces (blue and purple) for the wavefunction of the Si–H bonding state. All isosurfaces in this work are shown for an isovalue of $\pm 0.1 \text{ a}_0^{-3/2}$.

B. Si–H model

As a host material for studying the Si–H bond, we use α -quartz, a common SiO_2 polymorph, which crystallizes in a trigonal lattice with space group $P3_221$. Although α -quartz does not include the structural disorder present in a- SiO_2 , it provides a well-defined tetrahedral SiO_2 network in which the local hole-capture mechanism can be studied in isolation. Related E' centers have also been shown to behave similarly in α -quartz and a- SiO_2 [33], further supporting the use of α -quartz as a model system for the mechanism considered here. After performing geometry and cell relaxations within our DFT simulations, the primitive unit cell of α -quartz has the lattice parameters $a = b = 4.937 \text{ \AA}$ and $c = 5.431 \text{ \AA}$ in good agreement with established experimental values ($a = b = 4.912 \text{ \AA}$, $c = 5.404 \text{ \AA}$) [34]. We used an exact exchange fraction of $\alpha = 0.35$ for the hybrid functional in order to match the experimental bandgap of $E_{g, SiO_2} = 8.9 \text{ eV}$ [10]. For all our calculations, we first transformed the primitive unit cell into an orthorhombic conventional cell containing 18 atoms. A $3 \times 3 \times 2$ multiple of this conventional cell was then constructed to obtain a supercell with 324 atoms and lattice dimensions $a = 14.811 \text{ \AA}$, $b = 16.292 \text{ \AA}$, and $c = 17.093 \text{ \AA}$, for which we used Γ -point sampling of the Brillouin zone.

Following recent work studying DBs in bulk semiconductors [35], we proceed by removing a single Si–O unit in the middle of the supercell resulting in one Si- and three O-DBs, each of which is passivated by hydrogen. We manually puckered [36] the Si–H bond, i.e., displaced the Si atom through the plane of its neighboring O atoms so that the Si–H bond “points” in the opposite direction. This avoids interactions with the nearby OH groups and allows us to model the Si–H bond in a more bulk-like SiO_2

environment. However, our calculations show that both puckered and unpuckered configurations dissociate similarly upon hole trapping. A subsequent geometry optimization is performed, leading to the structure depicted in Fig. 2. As can be seen, the 3 OH-groups arrange themselves in a ring due to the formation of weak electrostatic hydrogen bonds ($\text{O}-\text{H}\cdots\text{O}$). This procedure results in an isolated Si—H bond, which does not interact with the OH groups on the opposite side as indicated by the isosurfaces of the corresponding molecular orbital. Contrary to the Si—H bond, the O—H bonds do not introduce any states in the bandgap since they are below the SiO_2 VBM.

C. Nonradiative capture by multiphonon emission

In order for an initially delocalized carrier in the CB or VB to get trapped at a defect site, a perturbation is required, which couples the wavefunction of the isolated defect in the bandgap to the carrier wavefunction, leading to a nonvanishing transition matrix element. Within the methodology developed by Alkauskas *et al.* [24], the total charge capture coefficient C from an initial electronic state $|\psi_i\rangle$ to a final state $|\psi_f\rangle$ due to MPE is determined by Fermi's Golden Rule and is given by [24,37]

$$C(T) = \frac{2\pi}{\hbar} fV |W_{if}|^2 \sum_{m,n} w_m(T) |\langle \chi_{im} | \hat{Q} - Q_0 | \chi_{fn} \rangle|^2 \times \delta(E_{im} - E_{fn}). \quad (1)$$

Here, f denotes the Sommerfeld parameter, which accounts for the electrostatic attraction or repulsion of carriers to a charged defect. Since we are looking at hole-trapping of an initially neutral Si—H bond, this parameter is simply $f = 1$. By including the supercell volume V in Eq. (1), we obtain the volume-independent capture coefficient C , rather than a capture rate that depends on the chosen supercell size.

The movement of the nuclei is governed by the potential energy curves (PECs) $V_{\{i,f\}}(Q)$ in the initial and final state as a function of the one-dimensional configuration coordinate (CC) Q , which linearly interpolates between the minimum configurations of both states in mass-weighted coordinates (see also Sec. III B). From these potentials, the vibrational modes $\chi_{\{im,fn\}}(Q)$ and their eigenenergies $E_{\{im,fn\}}$ can be calculated by numerically solving the Schrödinger equation for the nuclei. The thermal occupation $w_m(T)$ of each individual vibrational mode m in the initial state follows a Bose-Einstein distribution. The configuration of the initially neutral Si—H bond is denoted as Q_0 . Using first-order perturbation theory, the electron-phonon matrix element W_{if} can be expressed as [38]

$$W_{if} = \left\langle \psi_i \left| \frac{\partial \hat{H}}{\partial Q} \right| \psi_f \right\rangle = (\epsilon_f - \epsilon_i) \left\langle \psi_i \left| \frac{\partial \psi_f}{\partial Q} \right\rangle, \quad (2)$$

where $\epsilon_{\{i,f\}}$ denotes the single-particle Kohn-Sham (KS) energies of the initial and final electronic state. In this formulation, only the wavefunctions and their derivatives are required and not the derivative of the KS Hamiltonian $\hat{H}$, allowing for a simple evaluation of the matrix element using finite differences. Since CP2K employs highly efficient but position-dependent Gaussian basis sets, we evaluate the matrix element in real space using finite displacements $\delta Q = 0.05 \sqrt{\text{amu}} \text{ \AA}$, where amu stands for the atomic mass unit.

D. Energetics

Evaluating the vibrational wavefunctions and subsequently the capture coefficient requires calculating the PECs $V_{\{i,f\}}(Q)$ in *both* charge states. However, when comparing total energies from differently charged supercells, additional alignments and corrections have to be accounted for, which are encapsulated in the concept of defect formation energies. Within the established supercell approach [39], the formation energy of a defect configuration X_q in charge state q is given by

$$E_f[X_q] = E_{\text{tot}}[X_q] - E_{\text{tot}}[\text{bulk}] - \sum_i n_i \mu_i + q(\epsilon_{\text{VBM}} + E_F) + \Delta_q, \quad (3)$$

where $E_{\text{tot}}[X_q]$ and $E_{\text{tot}}[\text{bulk}]$ denote the total energies of the defective and the pristine bulk supercell, respectively. Since we are interested in the dissociation of a single preexisting Si—H bond and not in its original formation, we replace $E_{\text{tot}}[\text{bulk}]$ with $E_{\text{tot}}[\text{Si} - \text{H}^0]$. Thus, the neutral Si—H bond as depicted in Fig. 2 serves as an energy reference. The formation energy of the charged defect also depends on the Fermi level E_F of the interacting carrier reservoir. E_F is given with respect to the VBM of the host material, which is approximated by the energy ϵ_{VBM} of the highest occupied KS state in the bulk. The charge-dependent term Δ_q combines corrections for electrostatic self-interaction from image charges in neighboring periodic cells, with an alignment of the average Hartree potential across the different supercell calculations. Here, we employ the Freysoldt-Neugebauer-Van de Walle correction scheme [40] as implemented in the SXDEFECTALIGN package [41] to obtain Δ_q . The chemical potential μ_i accounts for the energy required to add ($n_i > 0$) or remove ($n_i < 0$) atoms of species i to construct the defect of interest. For the purposes of this work, we assume the chemical potential of H simply to be given by $\mu_H = \frac{1}{2} E_{\text{tot}}[\text{H}_2]$.

The formation energies determine the relative thermodynamic stability of different defect states as a function of E_F . As depicted in Fig. 3, the thermodynamic charge-state transition level (CTL) $\epsilon(q, q')$ of two charge states q and q' is defined as the Fermi level at which both states are

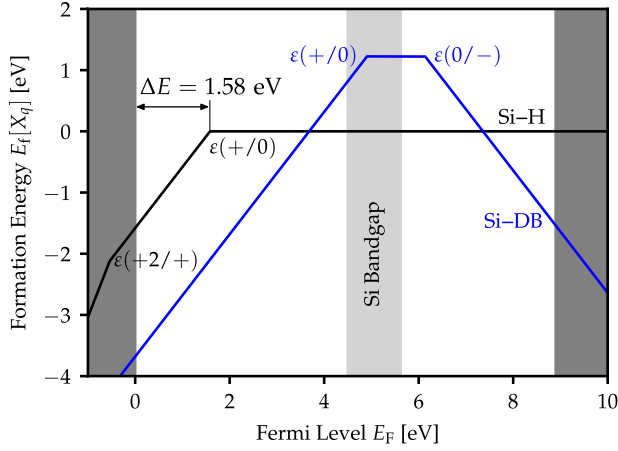


FIG. 3. Formation energies and charge-state transition levels of the Si—H bond and an isolated Si-DB within the SiO₂ bandgap. The Si—H bond has a hole trap level at $\varepsilon(+ / 0) = 1.58$ eV above the SiO₂ VBM and thus is able to capture a hole from the VBM. The Si-DB has both hole and electron trap levels in the vicinity of the band edges of the Si channel and hence can act as an amphoteric charge trap, potentially causing device instability.

equally stable. Hence, $\varepsilon(q, q')$ marks the boundary between different charge stability regions. The CTL also determines the relative energetic alignment ΔE of the PECs in the CC diagram for a particular transition. Here, we are primarily interested in the process of trapping a hole from the SiO₂ VBM at $E_F = 0$ eV in the Si—H bond. In this case, we simply obtain $\Delta E = \varepsilon(+ / 0)$ as can be seen in Fig. 3. We note that the CTLs are independent of the particular choice of μ_H , since they depend only on formation energy differences.

III. RESULTS

A. Electronic structure of the Si—H bond

As described in Sec. II B, we prepared an isolated Si—H bond in an α -quartz supercell. The Si—H bond introduces a doubly occupied KS bonding state 0.39 eV above the SiO₂ VBM (Fig. 1). Hence, it can in principle capture up to two holes from the top of the SiO₂ VB. However, just considering the occupation of the frozen KS states of the defect neglects any electronic or ionic relaxation associated with the charge transition. Looking instead at the charge transition levels of the Si—H bond (which include all these relaxations) in Fig. 3, we see that the $(+ / 0)$ transition occurs at $\varepsilon(+ / 0) = 1.58$ eV within the oxide bandgap. For a hole at the VBM, the Fermi level $E_F = 0$ eV is below $\varepsilon(+ / 0)$, meaning the positive charge state (trapped hole) of the Si—H bond is indeed thermodynamically favorable. In contrast, the $\varepsilon(+2 / +)$ CTL for trapping a second hole is 0.54 eV below the VBM. As will be discussed in the next section, capturing a single hole is sufficient to cause a spontaneous dissociation of the Si—H bond.

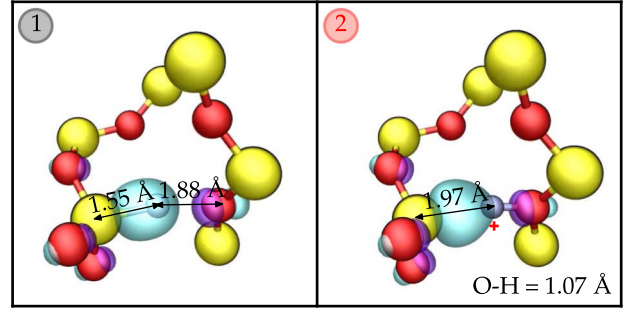


FIG. 4. Configurations of the neutral Si—H bond (1) and after capturing a hole (2), whereby the H becomes H⁺, as symbolized by the red plus sign and attaches to the nearest bridging O atom facing the formed dangling bond. Note that state (1) is identical to the initial configuration presented in Fig. 2.

After capturing a hole, the H moves toward the closest nearby bridging O atom as shown in state 2 of Fig. 4. During this process, the Si—H bond length increases from 1.55 to 1.97 Å, while the charge center of the remaining electron is shifted closer to the Si atom, reducing its distance from 1.36 to 0.95 Å. This indicates that the captured hole results in the H atom becoming H⁺, while the remaining unpaired electron forms a O₃ = Si· dangling bond. The H⁺ attaches itself to the partially negatively charged bridging oxygen atoms.

Note that the DB defect (state 2) is not yet an isolated Si-DB (see state 0 in Fig. 1), and its KS levels are significantly lower than in the isolated DB due to the presence of H⁺, as can be seen in Fig. 1. However, as will be discussed in Sec. III C, the H⁺ can easily diffuse away, leaving behind an isolated neutral E' center. In our simulation setup, the isolated Si-DB can be created by simply removing the H⁺ from the simulation cell followed by a geometry relaxation. Contrary to its Si—H precursor, the E' center has a hole trap level $\varepsilon(+ / 0) = 4.89$ eV and an electron trap level $\varepsilon(0 / -) = 6.13$ eV in the upper half of the SiO₂ bandgap and hence close to the band edges of the Si channel (Fig. 3). The Si-DB is thus amphoteric and susceptible to charge trapping from the channel and therefore can play a role in device reliability.

B. Hole trapping and bond dissociation

While adding a hole to the simulation reveals the dissociation of the Si—H bond, understanding the actual hole capture process and its dynamics requires the use of the MPE framework outlined in Sec. II C. As can be seen from Fig. 5 (bottom), the PEC of the positive complex is strongly anharmonic in contrast to the PEC of the neutral Si—H bond. We attribute this anharmonicity to the fact that the interaction between the bridging O atom and H⁺ is mainly governed by long-range electrostatic attraction rather than a short, stiff covalent bond, leading to a strongly nonparabolic PEC along the dissociation path.

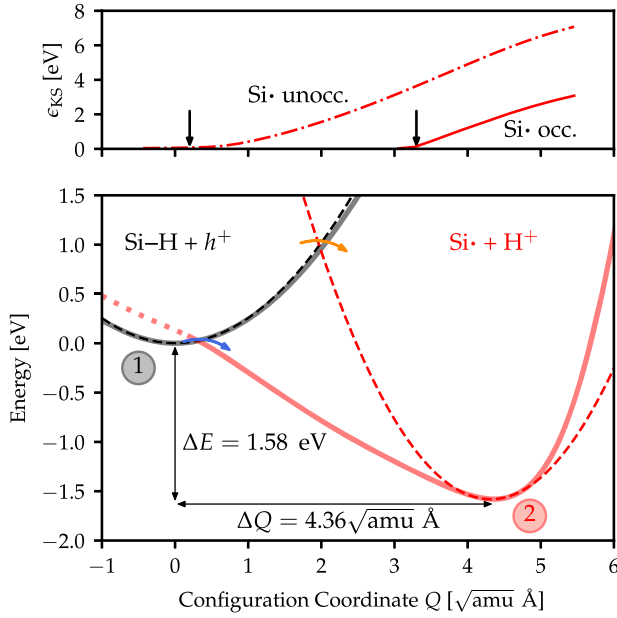


FIG. 5. Top: Evolution of the occupied and unoccupied Kohn-Sham levels (see also Fig. 1) associated with the Si dangling bond containing a single electron (state 2) during structural relaxation following hole capture. The arrows indicate the crossing of these levels with the SiO_2 VBM. Bottom: PECs for the hole capture process from state 1 to 2 in Fig. 4. The blue and orange arrows depict the classical transition points for the anharmonic PECs (solid lines) and their harmonic approximation (dashed lines), respectively; see also Fig. 6.

Additionally, the occupied Si-DB state containing a single electron crosses the SiO_2 VBM close to the minimum of the positive PEC [Fig. 5 (top)]. In this configuration, it becomes strongly hybridized with the valence-band states, which may further enhance the anharmonicity.

Note that the added hole stays localized at the defect as long as the unoccupied DB state remains within the SiO_2 bandgap, hence the potential energy of the correct electronic structure can still be obtained from ground-state DFT calculations. The emergence of this unoccupied state out of the SiO_2 valence-band manifold into the bandgap [see Fig. 5 (top)] causes the hole to localize on the DB already near the minimum of the neutral Si-H potential. When the unoccupied KS state crosses into the VB, however, the hole delocalizes at the VBM leading to a change of the electronic structure as indicated by the dotted PEC in Fig. 5 (bottom). For the purposes of calculating the hole capture coefficient, however, the ground-state DFT treatment is sufficient, since the invalid portion of the PEC (dotted line in Fig. 5) is already beyond the PEC crossing point, which determines [42] the capture rate in Marcus theory [43] (the classical limit for MPE transitions).

In order to evaluate the hole capture coefficient given in Eq. (1), the vibrational modes χ_{im} and χ_{fn} were calculated

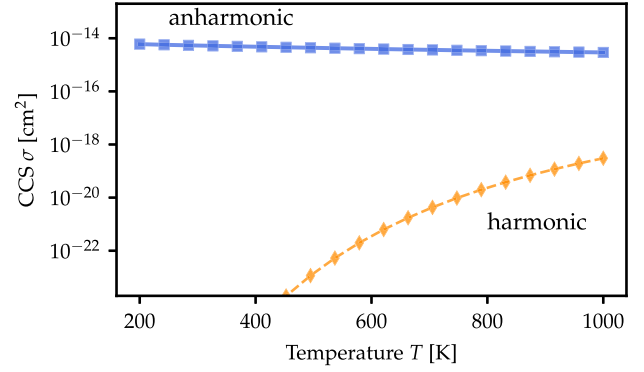


FIG. 6. Hole capture cross sections for the Si-H bond using the anharmonic and harmonic potential energy curves. In the anharmonic case, the capture cross section is much larger and almost temperature independent due to the very small classical transition barrier.

by solving the vibrational Schrödinger equation numerically up to $m = 40$ and $n = 80$. The electron-phonon coupling element was determined to be $W_{if} = 26 \text{ meV \AA} \sqrt{\text{amu}}$. We calculated the capture coefficients both for the anharmonic PECs as obtained from evaluating the DFT energies along the configuration coordinate Q , as well as for the typically employed harmonic approximation (dashed lines in Fig. 5). For the harmonic oscillators, we obtained the vibrational frequencies $\hbar\Omega_i = 46 \text{ meV}$ and $\hbar\Omega_f = 62 \text{ meV}$.

To facilitate comparison with experiment, we calculated the CCS as $\sigma = C/\langle v_{\text{th}} \rangle$, where $\langle v_{\text{th}} \rangle = \sqrt{k_B T/m_h^*}$ denotes the average thermal velocity of the hole at the VBM. The effective mass of the hole was assumed to be $m_h^* = 7.5m_0$ [44]. For practical computations of the capture coefficient, the Dirac- δ in Eq. (1) is broadened using a Gaussian with $\sigma = 20 \text{ meV}$, corresponding to roughly $0.5\hbar\Omega_i$ in order to avoid artificial peaks in the lineshape function [37]. The resulting CCSs are depicted in Fig. 6. The CCS from the anharmonic PECs is roughly temperature independent in a wide temperature range with a value of $\sigma = 6 \times 10^{-15} \text{ cm}^2$ at $T = 300 \text{ K}$, in good agreement with the experimentally established value [12] of $\sigma = 3 \times 10^{-14} \text{ cm}^2$.

In contrast, the CCS from the harmonic approximation is orders of magnitude smaller and strongly temperature dependent. This stark difference can be easily understood in the classical picture of MPE transitions, in which the overall transition rate and its thermal activation are governed by the classical barrier given by the crossing point of the involved PECs. The classical barrier for capturing a hole is 0.99 eV for the harmonic PECs, but only 23 meV for the anharmonic PECs. In the anharmonic case, the barrier is so low that the largest vibrational overlap already stems from the ground state and the first excited state of the neutral Si-H bond, leading to the observed very weak temperature dependence. The

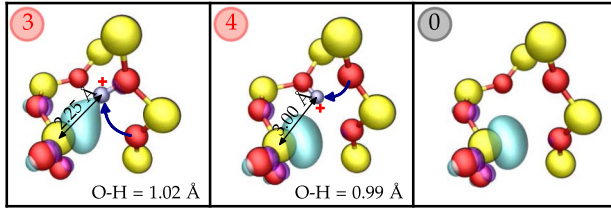


FIG. 7. Migration steps of H^+ after hole capture and Si-H bond dissociation. Starting from state 2, the migration path away from the Si-DB proceeds via a nearest-neighbor hopping (3), followed by a cross-ring hopping (4). After the cross-ring hopping step, the H^+ is sufficiently far from the Si-DB that its local geometry and charge distribution closely resemble those of an isolated Si-DB (0).

comparison between the harmonic and anharmonic model shows that the large hole capture cross section observed in experiments can only be explained when taking the pronounced anharmonicity of the Si-H bond dissociation into account.

C. H^+ migration

After the hole capture event and the subsequent dissociation, the defect is in state 2 as shown in Fig. 4. While in this state, the Si dangling bond has already formed, its electronic structure is still quite different from an isolated DB due to the interaction with the nearby proton, as can be seen in Fig. 1. We therefore investigate the migration path of H^+ away from the dangling-bond site using the NEB method, focusing on a specific path starting from the newly formed Si-DB and showing that the migration is not significantly impeded by the presence of the dangling bond.

The considered migration path is shown in Fig. 7, and the corresponding barriers are reported in Fig. 8. After the initial hole trapping process, the H^+ hops to a nearest-neighbor bridging-O (state 3) with a barrier of 0.61 eV. This is significantly lower than the reported average 0.99 eV barrier for the same hopping process in a-SiO₂ [21] without the presence of the Si-DB. In this state, the interaction between the DB and H^+ remains considerable. This is reflected in the elongated O-H⁺ bond length of 1.02 Å, compared to the equilibrium distance of 0.99 Å between a bridging O and H^+ in otherwise pristine α -quartz (i.e., without a nearby DB), as well as in the distorted charge distribution of the Si-DB. The lowest energy transition leading further away from the DB is found to be a cross-ring hopping (state 4). This transition has a barrier of 0.52 eV with respect to state 3, which is in good agreement with the previously reported average value of 0.55 eV for cross-ring hopping in a-SiO₂ [21]. In state 4, the distance of H^+ to the Si carrying the DB is already 3.00 Å, indicating that the interaction with the DB is weak. While the KS energy levels of the DB are still affected by

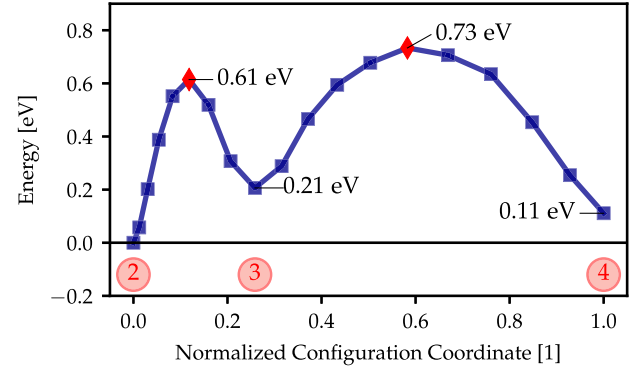


FIG. 8. Potential energies along the H^+ migration path obtained from NEB calculations. The states are defined as in Fig. 1, and all energies are given with respect to state 2.

the presence of H^+ , the charge distribution of the DB is mostly undistorted compared to its isolated form (state 0) and the O-H⁺ bond length already reaches its corresponding bulk value of 0.99 Å at this distance from the DB. Based on these observations, we conclude that the further migration of H^+ will not be significantly different from diffusion in bulk.

To check whether H^+ is thermodynamically bound to the Si-DB, we also considered a configuration in the same supercell where H^+ is attached to a distant bridging O atom (about 8 Å away from the Si-DB). We found this state to be only 36 meV higher in energy than state 2, indicating that H^+ is at most weakly bound to the DB. Since the calculated barriers can also be easily overcome at room temperature, hole capture at the Si-H bond thus leads to the release of H^+ , which can then diffuse freely throughout the oxide.

D. Discussion

Our defect model in α -quartz reproduces several key features previously reported for defects in a-SiO₂. For instance, the Si-DB is amphoteric and susceptible to charge trapping from the Si channel in a device. It can therefore impact device reliability in close analogy to other dangling-bond-type defects in SiO₂, such as the hydrogen bridge and the hydroxyl- E' center [7,45,46]. Furthermore, the barriers for H^+ migration in α -quartz generally fall into the same overall range determined for a-SiO₂ in earlier investigations [21,22]. However, in our model the nearest-neighbor hopping from state 2 to state 3 shows a barrier of 0.61 eV, which is significantly smaller than the reported average value of 0.99 eV for the same hopping process in a-SiO₂ without a nearby Si-DB [21], suggesting that the presence of the Si-DB facilitates this particular transition. The subsequent cross-ring hop from state 3 to state 4 has a barrier of 0.52 eV, in very good agreement with the previously reported average of 0.55 eV for cross-ring hopping in a-SiO₂ [21]. Moreover, as in a-SiO₂ [22],

the proton continues to influence the electronic structure of the DB even at larger distances. The presence of H^+ still lowers the Si-DB Kohn-Sham levels by 0.5–0.6 eV relative to an isolated DB, as seen by comparing state 4 and 0 in Fig. 1. Taken together, these trends show that the Si-DB/ H^+ complex in crystalline α -quartz behaves in a similar way to its amorphous counterparts, while providing a well-defined structural reference.

Earlier theoretical studies in a-SiO₂ investigated hole-induced Si-H dissociation by “injecting” a hole [22,25], i.e., removing an electron from the highest occupied state followed by a subsequent ionic relaxation. In the CC diagram shown in Fig. 5, this would correspond to a vertical transition to the positive PEC with the geometry being fixed at the minimum of the neutral Si-H PEC (state 1 at $Q = 0$), after which the system relaxes along the positive PEC. In amorphous models, this procedure yields both barrierless (“spontaneous”) dissociations and dissociations with small thermal barriers up to 0.5 eV, reflecting the distribution of local environments [22,25]. Our α -quartz results are consistent with this qualitative picture in the sense that, once the system is placed on the positive PEC, the relaxation can proceed directly toward a dissociated minimum (state 2). However, the vertical hole-injection scheme is best viewed as a tool for identifying accessible configurations in the charged state and does not by itself determine the physical transition rate. It does not describe how the system *reaches* the positive PEC in the first place. In this sense, the notion of a “spontaneous” transition within the injection picture has no direct kinetic meaning. The actual evolution from state 1 to state 2 proceeds along the PECs via nonradiative multiphonon emission with a finite rate, i.e., by crossing the barrier along the configuration coordinate rather than by an instantaneous vertical jump. The present work advances beyond this simple injection picture by treating this hole capture process quantitatively within the established MPE framework, thereby providing capture rates and cross sections that are not accessible by simply injecting a hole.

These kinetic conclusions also connect to the established understanding of radiation damage in MOS structures, where holes in the oxide and mobile hydrogen contribute to interface-state generation at Si/SiO₂ interfaces [11,16,17]. Since the calculated capture cross section is large and nearly temperature independent, irradiation-induced E' -center formation at susceptible bulk Si-H precursor sites is unlikely to be effectively suppressed by lowering the temperature. Mitigation should therefore target a reduction in excess hydrogen-related precursor sites in the oxide bulk, while preserving the hydrogen needed for interface passivation [16].

IV. SUMMARY AND CONCLUSION

We conducted a first-principles analysis of the dissociation of Si-H bonds in silicon dioxide (SiO₂) induced by

hole capture. This process is relevant to the reliability of silicon-based MOS transistors, because ionizing radiation generates electron-hole pairs and released H^+ can travel to the Si/SiO₂ interface and depassivate dangling bonds. Our computational approach, which combines DFT with non-radiative capture by MPE theory, allowed us to investigate the electronic structure, hole trapping dynamics, and the subsequent dissociation of a prototypical Si-H bond in α -quartz. This goes beyond previous studies that only injected the hole into the Si-H bond within the simulation, without considering the actual capture process from the top of the SiO₂ valence band.

Our findings demonstrate that Si-H bonds in SiO₂, although highly stable under normal conditions, can be readily dissociated upon capturing a hole from the SiO₂ valence band, which can be excited by ionizing radiation. The efficient hole capture process is facilitated by the pronounced anharmonicity of the Si-H bond dissociation, leading to an effective hole capture cross section of $\sigma = 6 \times 10^{-15} \text{ cm}^2$, which is in good agreement with experimental observations. This dissociation results in the formation of a positively charged proton (H^+) and a paramagnetic E' center, a defect that can significantly impact the electronic stability of the SiO₂ layer due to its amphoteric charge trapping behavior with trap levels close to the valence- and conduction-band edges of the Si device channel.

Furthermore, we explored the migration path of the resulting H^+ ion away from the Si dangling bond site. Our calculations indicate that H^+ can migrate away with relatively low-energy barriers, leaving behind an isolated E' center.

In conclusion, our study provides detailed insights into the mechanisms of Si-H bond dissociation and subsequent defect formation in SiO₂ under hole injection conditions. These findings not only support previous experimental results but also contribute to a deeper understanding of the processes that affect the long-term reliability of MOS devices and the degradation processes of the gate dielectric due to irradiation.

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DATA AVAILABILITY

The atomic structures corresponding to states 0–4 in Fig. 1 and an exemplary CP2K input file are available in the Zenodo repository (Ref. [47]).

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