Charging and Discharging of Oxide Defects in Reliability Issues

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***Abstract*— Negative Bias Temperature Instability (NBTI) has been recognized as a major reliability challenge years ago but a detailed microscopic understanding of the mechanisms governing NBTI is still missing. It appears to be very well established that depassivation of dangling bonds at the interface combined with diffusion of hydrogen may play a crucial role in this context. Some authors have argued that charging defects via tunneling also constitutes an additional contribution to this phenomenon. Conventionally, tunneling levels are believed to remain at fixed positions within the oxide bandgap regardless whether they are occupied or not. From a theoretical point of view, defect energy levels shift within the silicon dioxide bandgap due to charging or discharging. As a result, defect levels for tunneling into and out of a trap have to be distinguished. On the basis of this understanding of trapping, defects can be categorized as fixed charges, switching oxide charges, interface traps or other types of defects. In this study, we conduct an investigation on the energetics and the tunneling dynamics of a series of individual defects suspected to contribute to NBTI and deduce their behavior.**

I. Introduction

The existence of traps in dielectrics of semiconductors has been proven by plenty of investigations — in particular Electro-Paramagnetic-Resonance (EPR) measurements allow the identification of a large number of defects [1, 2]. Several experimental studies provide convincing indications of electron- or hole trapping in a-$\mathrm{SiO_2}$ during bias temperature stress or exposure to irradiation [3]. For instance, Zhang has proposed two types of traps in $\mathrm{SiO_2}$: Cycling Positive Charges (CPC) which can repeatedly exchange electrons with the interface but their total amount remaining unaffected by variations of the temperature. For a switching bias, they give rise to an ozillating behaviour in the monitored time evolution of oxide charges. The other defects, the so-called Anti-Neutralization Positive Charges (ANPC), forms a constant background which decreases as the temperature is raised. Lelis [3] conducted an annealing study on irradiated samples and found an accelerated annealing of elevated temperatures. This phenomenon is traced back to a defect level above the Si conduction band edge so that high energetic electrons are required for discharging of these defect (also termed switching traps). Various proposed models hold these distinct traps at least partially responsible for reliability issues [4] such as Negative Bias Temperature Instability (NBTI) and Hot Carrier Injection (HCI), but they still require of a fundamental, physical proof. The majority of these models relies on defect energies which remain at the same position within the oxide bandgap irrespective of their charge state. However, defect levels are in fact subject to a shift after charging or discharging. The origins are twofold: First, the new charge changes the Coulomb forces that determines the position of the energy levels. Second, the atoms proximate to the defect undergo a structural relaxation accompanied by strengthening, weakening, or even disrupting bonds. According to the Franck-Condon principle [5], this shift of energy levels occurs within femtoseconds compared to the considerably larger time constants observed for tunneling. In other words, the atomic configuration will adopt the new charge state before a new tunneling process can change the charge state of this defect again. This concept of charging and decharging has not received much attention to date, but has important implications on the tunneling kinetics in a-$\mathrm{SiO_2}$ as will be shown in the following.

II. Method

The issue of defect levels can be tackled within the framework of first-principles simulations. Theoretical investigations based on a more detailed understanding of trapping have already been undertaken using a crystalline structure for silicon dioxide (c-$\mathrm{SiO_2}$)[6–8]. At this point, we want to stress the fact that it is necessary to take the amorphous nature of silicon dioxide (a-$\mathrm{SiO_2}$) into account. As highlighted in [9, 10], crystalline structures used in theoretical examinations do not succeed in reproducing the properties of silicon dioxide in a satisfactory manner. Convincing support of this argument is provided through investigations on thermal oxidation. $\mathrm{O_2}$-molecules encounter a spread of barriers to migrate from one void to the next in amorphous silicon dioxide. This distribution of barriers determines the activation energy for the diffusion process [11, 12]. In contrast to that, $\mathrm{O_2}$-molecules have only single-valued barriers to overcome in a crystalline structure. The need to mimick the oxide with a-$\mathrm{SiO_2}$ is also supported by the stability of the E'_γ center depending on the local surrounding silica network. [10] In the following, we give an overview of the simulation approach used to obtain defect energy levels. The method of choice regarding the evaluation of defect levels is density functional theory (DFT). To reduce the computational costs, an empirical potential molecular dynamical (MD) has been employed for the production of a-$\mathrm{SiO_2}$. The Si- and O atoms are placed randomly within the simulation cell respecting exclusion radii as to avoid any overlap between the atoms. The size of the simulation cell (11.79 Å) has been chosen to exactly match the mass density ($2.19\,\mathrm{g/cm^3}$) observed experimentally. Taking this random

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structure as a starting configuration, the amorphous structure is allowed to evolve at high temperatures using a MD approach (BKS potential) [13–16]. The MD simulations comprise of an equilibration step at $3000\,\mathrm{K}$ for $30\,\mathrm{ps}$ with a timestep of $1\,\mathrm{fs}$ which was followed by a quenching step to $0\,\mathrm{K}$ for $30\,\mathrm{ps}$ with a timestep of $1\,\mathrm{fs}$. To prepare the amorphous samples for subsequent first-principles calculations, structural minimization, based on DFT simulations with the same exchange-correlation potential as used later again, has been performed. Since edge-sharing tetrahedra are unfavored from an energetic point of view, samples containing these edge-sharing tetrahedra are excluded from further investigations. The remaining samples exhibit no miscoordination. Pair-correlation functions, angle distributions and the ring-distribution have been evaluted, to make sure that the obtained samples correspond to a-$\mathrm{SiO_2}$. Perfect agreement has been achieved with previously published results [14–16] (see Table I). The exchange-correlation

	$d_{\mathrm{Si-O}}$	$d_{\mathrm{O-O}}$	$d_{\mathrm{Si-Si}}$	$\phi_{\mathrm{Ox-Si-Ox}}$	$\phi_{\mathrm{Si-Ox-Si}}$
Here	1.64	2.66	3.08	109.42	142.62
[14]	1.62	2.64	3.10	109.6	142.0
[15]	1.63	2.67	3.11	109.4	146.8
[16]	1.62	2.68	2.98	109	136

TABLE I

COMPARISON OF THE CHARACTERISTIC PROPERTIES OF THE PRODUCED a-$\mathrm{SiO_2}$. $d_{\mathrm{Si-O}}$, $d_{\mathrm{O-O}}$ AND $d_{\mathrm{Si-Si}}$ DENOTE THE FIRST MAXIMA IN THE APPROPRIATE PAIR-CORRELATION FUNCTION. $\phi_{\mathrm{Ox-Si-Ox}}$ AND $\phi_{\mathrm{Si-Ox-Si}}$ GIVE THE MAXIMUM OF THE APPROPRIATE ANGLE DISTRIBUTION IN EXCELLENT AGREEMENT WITH PUBLISHED VALUES. [14–16]

kernel used in our DFT calculations (VASP [17–21]) is based on gradient corrections and the projector augmented waves method (PAW) is used to represent ion cores. The plane wave cut-off energy was set to $400\,\mathrm{eV}$. Structural optimization was achieved through a conjugate gradient algorithm which limits the force on each atom to be below $0.3\,\mathrm{eV/Å}$. Charged supercells were calculated introducing a homogeneous compensating background charge to ensure neutrality within the supercell. The use of a plane wave code implicitly involves periodic boundary conditions and implies interactions between periodically arranged defects. To minimize this effect, large supercells of a-$\mathrm{SiO_2}$ ($\sim 11.79\,\mathrm{Å}$) comprising of 36 $\mathrm{SiO_2}$ units (108 atoms) were chosen. The integration of the Brillouin zone is constricted to the Γ-point only. Defect levels for tunneling mechanisms (also referred to as switching levels or transition states) are calculated as the energy difference between two differently charged supercells. The atomic structure is kept fixed pertaining to the Franck-Condon principle.

$$\varepsilon^{+/0}[\mathrm{X}^+] = E_\mathrm{f}^0[\mathrm{X}^+] - E_\mathrm{f}^+[\mathrm{X}^+] \quad (1)$$

$$\varepsilon^{0/+}[\mathrm{X}^0] = E_\mathrm{f}^0[\mathrm{X}^0] - E_\mathrm{f}^+[\mathrm{X}^0] \quad (2)$$

$$\varepsilon^{-/0}[\mathrm{X}^-] = E_\mathrm{f}^-[\mathrm{X}^-] - E_\mathrm{f}^0[\mathrm{X}^-] \quad (3)$$

$$\varepsilon^{0/-}[\mathrm{X}^0] = E_\mathrm{f}^-[\mathrm{X}^0] - E_\mathrm{f}^0[\mathrm{X}^0] \quad (4)$$

The sign in E_f^q corresponds to the formation energy in the charge state q, where $[\mathrm{X}^q]$ denotes the equilibrium configuration. For the sake of clarity, the $\varepsilon^{+/0}$ energy level comes into play for positive defects (X^+) which should be neutralized. The $\varepsilon^{0/+}$ energy level applies to the inverse process when neutral defects (X^0) capture positive charge carriers. Analogous considerations hold true for the energy levels $\varepsilon^{-/0}$ and $\varepsilon^{0/-}$. Concerning the bandgap alignment, we used the same procedure as proposed in [6]. However due to the amorphous nature of $\mathrm{SiO_2}$, we found a valence band offset of approximately $2.6\,\mathrm{eV}$ consistent with valence band offsets extracted from [22–24]. Although a similar study on trap-assisted tunneling in c-$\mathrm{SiO_2}$ has been conducted [6], the impact of the amorphous nature of silicon dioxide on the tunneling levels has not been investigated up to date. The focus of this paper is placed on reexamining trap levels in an amorphous silica network. Based on the knowledge of the position of the defect levels (listed in Table II) within the silicon dioxide bandgap, a list of defects, suspected to be charged oxide traps in MOSFET structures, will be discussed. Finally, a classification of these defects has been carried out.

III. O VACANCY

In stoichiometric a-$\mathrm{SiO_2}$, Si atoms are connected via bridging O atoms. As depicted in Fig. 1, an oxygen vacancy ($\mathrm{V_O}$) can be pictured by the removal of a bridging O atom. The remaining dangling bonds originating from the neighboring Si atoms form a common bond of the typical bond length observed in silicon bulk. This bond (see Fig. 2) is associated with a trap level far below the silicon conduction band edge. The positively charged counterpart of the O vacancy is referred to as the E'_δ center. The removal of one electron causes a repulsion between both Si atoms, accompanied by a strong increase of the Si-Si bond length. However, the common bond still persists, giving rise to one defect level close to the silicon valence band edge. This bond experiences a strongly variing tensile force due to the amorphous nature of silicon dioxide which explains the wide spread of $0/+$ energy levels for the E'_δ center. For the O vacancy, the impact of the surrounding network can be neglected compared to the strength of the Si-Si bond. Concerning the tunneling dynamics, one has to differentiate between two cases: If the defect level $+/0$ is located below the silicon valence band edge, electrons residing in the substrate will tunnel into the defect. Therefore a tunneling process of an electron from the silicon valence band into the singly occupied defect state is allowed. For the reverse process, the defect level is already shifted downwards. Herefrom, the electron is unlikely to find a high energetic h^+ from the substrate. In short, this defect remains neutral if it is discharged once. In the case that the defect level $+/0$ is located above the silicon valence band edge, the process for neutralizing the defect is impeded. Then the tunneling dynamics also allow the buildup of positive charges within the silicon dioxide which can be categorized as fixed positive charges.

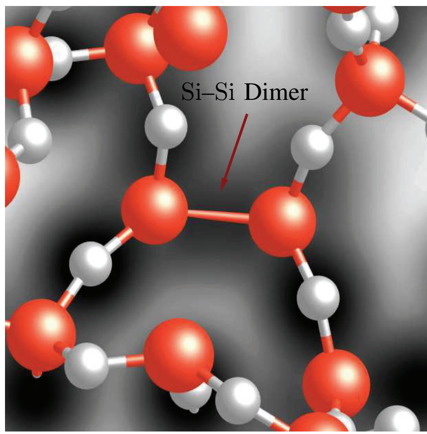

Fig. 1. Electron density plot of an oxygen vacancy. The reestablished Si-Si bond is indicated by a high charge density between the neighboring Si atoms. (Dark area ... high density; white area ... low density; big, dark spheres ... Si atoms; small, light spheres ... O atoms.)

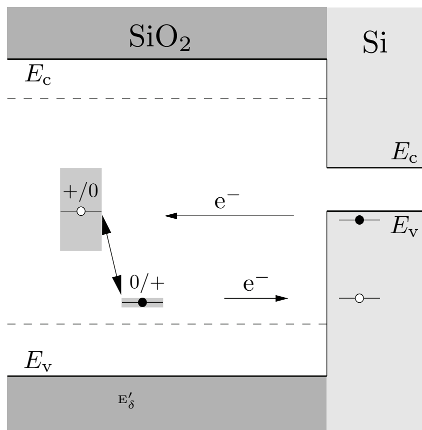

Fig. 2. Schematic of defect levels arising from O-vacancies or E'_δ centers, respectively. The $+/0$ levels ($\varepsilon_{+/0}$) are related to the capture of electrons. The $0/+$ levels ($\varepsilon_{0/+}$) apply to the inverse process, the emission of electrons. The arrow represents the Franck-Condon shift of energy levels and the spread of energy levels is indicated by the grey box. The wide spread of $\varepsilon_{+/0}$ levels requires a distinction whether the $\varepsilon_{+/0}$ levels lies above or below the silicon valence band edge.

IV. E'_γ CENTER AND VARIANTS

The existence of the E'_γ center, a stable partner of the E'_δ center has been confirmed by a wide range of both theoretical [9, 10] as well as experimental [26] studies. Starting from the E'_δ center, one side of this defect undergoes the well-established puckering: There, the Si atom emerging from the disruption of the Si-Si dimer moves through the plane defined by its three O-neighbors. This new configuration is stabilized via a weak bond of Si atom to a further nearby bridging O atom. On the other side of this defect, an unpaired electron in a dangling bond is left behind. The respective configuration is depicted in Fig. 3. In contrast to the O vacancy, the E'_γ center exhibits only a small spread in its defect levels because the dangling bond on the left hand side of Fig. 3 undergoes only little relaxation. The puckered side of the defect complex does not interfere with the dangling bond and in consequence does not affect its energetics. The levels for tunneling into $(+/0)$ or out of $(0/+)$ the traps lie close to the respective silicon band edges (see Fig. 4). Thus only a small thermal exciation of the majority charge carriers in the substrate is required for a tunneling process between the substrate and the defect. In this case, the band bending governs the concentrations of electrons in the silicon conduction band or holes in the silicon valence band, respectively, and in consequence controls the corresponding tunneling rates. In conclusion, the E'_γ defect is a good candidate for CPC which are capable of repeatedly exchanging electrons with the channel in MOSFETs [25]. Moreover, this defect configuration was already proposed by Lelis [3] for the temperature-dependent annealing behavior of traps in silicon dioxide. The temperature dependence in his model is related to a spin-triplet state which can capture electrons from the substrate by tunneling. At elevated temperatures, the concentration of excited electrons which are capable of undergoing a tunneling process is increased. As a result, the annealing of positively charged defects is accelerated. The proposed trap level of the Lelis model coincides with the defect level for neutralization in the present calculations. On the basis of shifting levels, the defect levels explaining the annealing behavior have been theoretically confirmed. As highlighted in [10], one group of E'_γ centers in a-SiO_2 (termed $E'_{\gamma 5}$ centers) collapses into the so-called dimer configuration after neutralization. The final structure coincides with that of an O vacancy. Identically to the situation of the E'_γ centers, the defect level starts at the same position above the silicon conduction band. However, after neutralization the respective energy level shifts down far below the silicon valence band edge as in the case of the O vacancy. Therefore once this defect is neutralized, it cannot be recharged again and will be annealed out permantently. Another variant of the E'_γ center is the E'_{74} center (depicted in Fig. 5) which has been extensively examined by Conley and Lenahan [26]. Its structure can be imagined by replacing one of the nearby O atoms with an H atom. Calculations on this defect show that the neighboring H atom does not affect the position of the defect levels originating from the dangling bond. As a result, this defect can also be categorized as a switching trap or a CPC. However, in some cases a bond between the H atom and another network atom could be observed, giving rise to additional defect levels below the silicon valence band edge.

V. H BRIDGE

In addition, we examined a hydrogenated variant of the E'_δ, center which is also referred to as the H bridge (see Fig. 6). In this case, the H atom places itself between both adjacent Si atoms of the E'_δ center. The H atom of this complex exhibits a symmetry in distances to both Si atoms, whereas this symmetry is broken in the neutral case. Therefore much structural relaxation is undergone which in turn explains the wide spread in defect energy levels. All defect levels (Fig. 7) are located within reasonable distance from silicon band edges

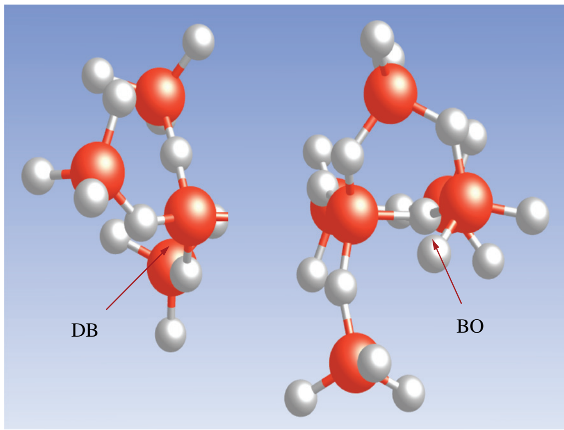

Fig. 3. Structure of an E'_γ center. The silicon atom on the left hand side carries an electron in the dangling bond (DB). The positively charged silicon atom on the right hand side is bonded to the back oxygen (BO). This atomic arrangement is also referred to as the puckered configuration.

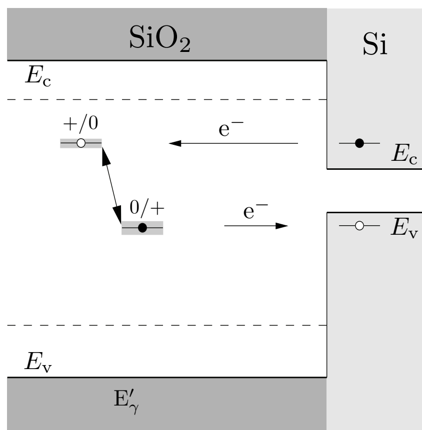

Fig. 4. Schematic of the defect levels originating from an E'_γ centers. The energy levels for the capture of electrons (+/0) as well as the energy levels for the emission of electrons (0/+) are found to lie close to the silicon conduction band or the silicon valence band, respectively.

in the energy scale. So all transistions between the substrate and the defect are allowed and therefore this defect will appear in all charged variants. As for the E'_γ center, the charge state of this defect depends on the band bending of the substrate. In summary, this defect can be classified as an interface-like trap exhibiting large time constants.

VI. H ATOM

In the context of NBTI, the H atom is of special interest, because it is available in appreciable amounts and should be investigated as a possible candidate for trapped charges. Many investigations have shown that hydrogen is indeed a prime suspect in reliability issues. Its configuration strongly differs with its charge state: The neutral H^0 atom resides in the middle of a void. The postive H^+ atom loosely binds to network O atoms (shown in Fig. 8) and the negative H^- atom attaches itself to network Si atoms. However, the energy levels of this defect are located too far away from the silicon band edges so

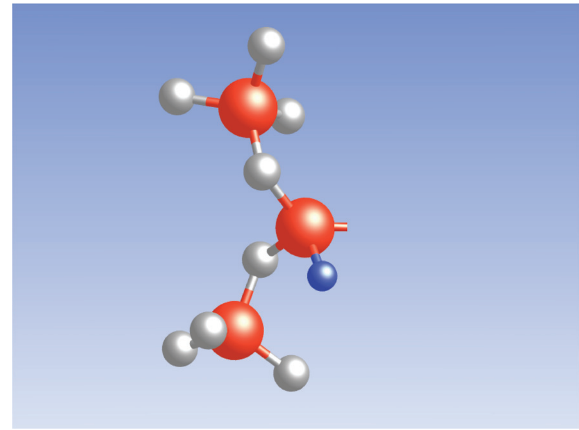

Fig. 5. Representation of an E'_{74} center. One of the neighboring O atoms is replaced by an H atom which shows a tendency to bond to a silica network atom. (Big, dark spheres . . . Si atoms; small, light spheres . . . O atoms; small, dark spheres . . . H atoms)

that exchanging electrons with the interface is impeded. The sole exception is the trap level 0/− for charging the hydrogen atom negatively. That is to say that charged H atoms keep their charge state. For the neutral H atom, the data in Fig. 9 suggest that the H atom slightly tends to take the negative charge state. At a first glance, this contradicts the findings of other groups [27–29] concerning the most stable charge state of the H atom being the proton. However, the reactivity of the H atom supports the thermodynamical point of view and attaches less importance to tunneling dynamics near the interface. For pMOSFETs, the silicon band edge is bent down associated with a decreasing density of electrons near the interface. Therefore a transition of an electron from the silicon into a defect becomes less likely.

	E'_δ	E'_γ	E'_δH	H
+/0	1.7 − 3.6 eV	3.9 − 4.1 eV	4.4 − 4.9 eV	4.9 − 5.1 eV
0/+	0.3 − 0.5 eV	2.1 − 2.4 eV	1.7 − 2.3 eV	0.3 − 0.9 eV
0/−			4.1 − 4.3 eV	3.2 − 4.4 eV
−/0			1.2 − 2.6 eV	0.9 − 1.2 eV

TABLE II
ENERGY TRAP LEVELS (+/0, 0/+, ETC.) RELATIVE TO THE THEORETICAL OXIDE VALENCE BAND MAXIMUM OF a-SiO_2. THE FIRST SIGN DENOTES THE EQUILIBRIUM CONFIGURATION OF THE DEFECT IN THE CORRESPONDING CHARGE STATE AND THE SECOND SIGN GIVES THE CHARGE STATE OF THE DEFECT FOR A GIVEN CONFIGURATION.

VII. CONCLUSIONS

We have carried out an investigation of the trapping and detrapping energy levels. For example, the E'_γ center should be considered as a defect capable of exchanging electrons with the interface. An O vacancy with a defect level below the Si bandgap is found to remain neutral whereas an O vacancy having a defect level within the Si bandgap can act as a fixed oxide charge. The H bridge can be classified as an interface-like trap with large time constants. For the

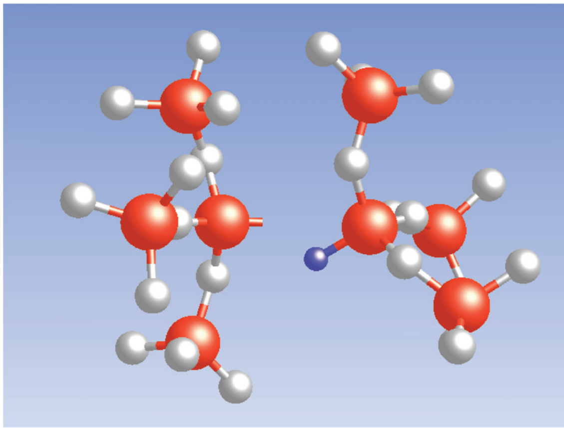

Fig. 6. Representation of the H bridge in the neutral charge state. For the postively charged defect, there arises a Si-H-Si bond chain. After neutralization this chain is disrupted yielding a dangling bond on the left hand side of this complex and a saturated dangling bond on the right hand side. In the case of a negatively charged H bridge, the Si-H bond is bent away from the dangling bond.

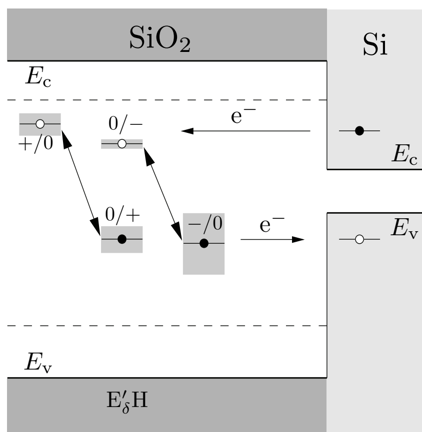

Fig. 7. Schematic of defect levels of an H bridge. All energy levels are located within a appropriate distance in the energy scale and allow an exchange of charge carriers in timescales of interest.

H atom, any trapping or detrapping mechanism is impeded except from charging the neutral H atom negatively. It is of utmost importance to take the distinct energy levels for tunneling into and out of defects into account for a successful description of the physics behind tunneling.

VIII. Aknowledgements

The authors gratefully acknowledge helpful discussions and comments from S.T. Pantelides, I.G. Batyrev, F. Mittendorfer, and G. Kresse.

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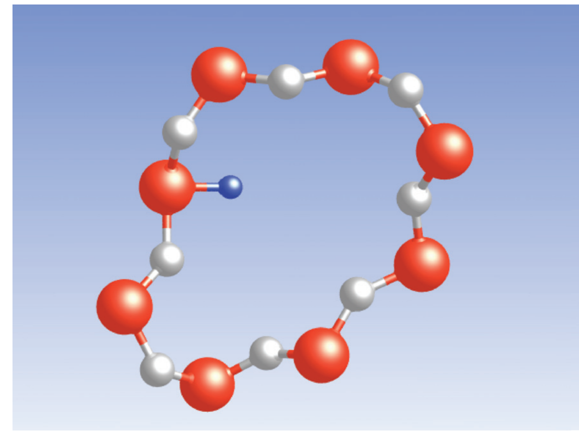

Fig. 8. Representation of a proton attached to the silica network. The H$^+$ attaches to the bridging O atom, the H^0 is situated in the middle of a void and the H$^-$ forms a weak bond to a network Si atom.

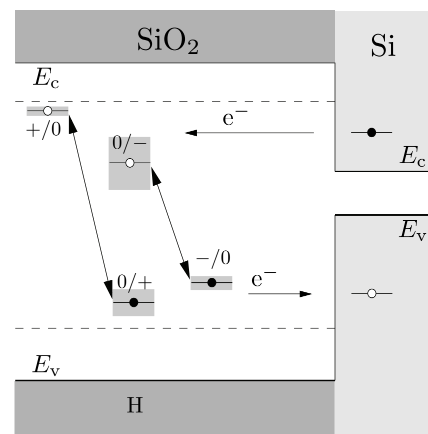

Fig. 9. Schematic of defect levels of the H atom. The energy levels for charging and discharging are far away from the respective silicon band edges. Only the energy levels $0/-$ for charging the H^0 postively allow transitions rate in a magnitude of interest.

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Questions and Answers

Q: Will the hydrogen stay at the E' delta H center? How strong is the hydrogen bond in the hydrogen bridge defect?

A: The hydrogen atom at the E' delta H center forms a bond with its two neighboring Si atoms. We investigated the stability of the positive hydrogen bridge performing molecular dynamics based on density functional theory. At a temperature of 300 K, neither of the Si-H bonds is observed to be disrupted. Therefore, the H atom stays in between the silicon atoms and the defect remains stable.

Q: Should it be a paramagnetic site?
A: A paramagnetic site requires an odd number of electrons in one orbital for a spin flip. Therefore, in the positively charged state of this defect, one will not detect an EPR signal. However, in the case of a neutral E' delta H center, the odd number of electrons allows a spin flip and will therefore give an EPR signal.

Q: Is this defect similar to the hydrogen coupled E' centers reported in the literature?
A: To the best of my knowledge, the literature refers to the 74 G doublet of the E' centers in this context. This defect which was investigated in this study has a different configuration than the E' delta H center and therefore its behavior presumably differs strongly.

Q: Do you think your calculations are consistent with the Lelis model?
A: Lelis proposed the E' gamma center as a candidate for switching traps and found approximately the same positions of trap levels as in the present study. These data even support the model of Lelis when the different physical origin of the upper trap level of the E' gamma center is accepted.

Q: How big is the unit cell (number of atoms) simulated to determine the energetics of defect?
A: In the literature simulations of defects are performed on supercells containing 72 atoms. The supercells under investigation in this study comprise of 108 atoms which is a number large enough to reduce the undesired effects stemming from the periodic boundary condition to a negligible extent.