

# First-Principles Investigation on Oxide Trapping

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## Abstract

We conduct a thorough investigation of the tunneling dynamics of oxide traps in a-SiO<sub>2</sub>, in particular of the E'<sub>δ</sub> center, the E'<sub>γ</sub> center, their hydrogenated counterparts, and the H atom. Based on these findings their behavior in the context of tunneling can be deduced. It is found that an E'<sub>γ</sub> center can exchange electrons with the Si bulk. The E'<sub>δ</sub> center shows two distinct behaviors induced by a spread in its tunneling levels. The H atom is not affected by the presence of an interface, whereas a H bridge may occur in every charge state.

## 1 Introduction

Defect levels of traps have long been the subject of numerous investigations. Several experimental studies provide convincing indications of electron- or hole trapping in a-SiO<sub>2</sub> during bias temperature stress or exposure to irradiation [1]. A large number of defects have been studied in literature [1, 2], either identified by their electro-paramagnetic-resonance (EPR) signal or by their atomic-scale configurations. However, the fact that defects undergo structural relaxation accompanied by a shift in their energy levels has not received much attention to date, but has important implications on the tunneling kinetics in a-SiO<sub>2</sub>. This issue can be tackled within the framework of first-principles simulations. Although a similar study for c-SiO<sub>2</sub> has been published [2], a detailed investigation addressing the variations of tunneling levels due to deviations of the local atomic arrangement in a-SiO<sub>2</sub> has not been performed up to date. The need to mimic the oxide with a-SiO<sub>2</sub> has been demonstrated by [3].

## 2 Method

For this purpose, simulations were done employing density functional theory (DFT) based on gradient corrections for the exchange-correlation functional and the projector augmented waves method (PAW) representing ion cores [4]. The plane wave cut-off energy was expanded up to 400 eV. Structural optimization was controlled through a conjugate gradient algorithm which limits the force on each atom to be below 0.3 eV/Å. Charged supercells were calculated introducing a homogeneous compensating background charge to ensure neutrality. 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-SiO<sub>2</sub> (~ 11.79 Å) comprising of 36 SiO<sub>2</sub> units (108 atoms) were chosen. The Brillouin zone was sampled at the Γ-point.

For production of a-SiO<sub>2</sub> an initial random configuration respecting exclusion radii between atoms was created applying an empirical potential method (BKS-potential). An equilibration step at 3000 K for 30 ps with a timestep of 1 fs was followed by a quench to 0 K for 30 ps with a timestep of 1 fs. Subsequently, a structural optimization using DFT was carried out and the resulting silica network was classified by pair-correlation functions, angle distributions and the ring-distribution, which are in perfect agreement with published data [5].

Defect levels for tunneling mechanisms (also referred to as switching levels or transition states) are calculated as total energy differences of supercells in their initial and final charge state. The atomic structure is kept fixed according to the Frank-Condon principle.

$$\varepsilon^{+/0}[X^+] = E_f^0[X^+] - E_f^+[X^+], \quad \varepsilon^{0/+}[X^0] = E_f^0[X^0] - E_f^+[X^0] \quad (1)$$

$$\varepsilon^{-/0}[X^-] = E_f^-[X^-] - E_f^0[X^-], \quad \varepsilon^{0/-}[X^0] = E_f^-[X^0] - E_f^0[X^0] \quad (2)$$

The sign in  $E_f^q$  corresponds to the formation energy in the charge state  $q$ , where  $[X^q]$  denotes the equilibrium configuration.

After a tunneling process, a defect is not in its equilibrium configuration any more due to changes in the electrostatics. This gives rise to structural relaxation and different energetics including a new transition state. In consequence, different levels for tunneling into a defect and out of a defect arise, as depicted in Fig. 3. Concerning the bandgap alignment, we used the same procedure as proposed in [2], but due to the amorphous nature of a-SiO<sub>2</sub> we found a bandgap offset of approximately 2.6 eV consistent with valence band offsets extracted from [6].

### 3 Results

The O-vacancy can be envisioned by removing a bridging O atom from the silica network, where the adjacent Si atoms reestablish a common bond. In the neutral charge state, the bond length of about 2.3 – 3.0 Å comes close to the typical Si bond length in c-Si. For the positively charged variant, which is also referred to as  $E'_\delta$  centers, both Si atoms repel each other without breaking their bond. Therefore this variant exhibits a longer bond length which expands to values varying from 2.7 Å to 3.2 Å. Irrespective of their spread associated with variations in their configurations, these structural parameters are in good agreement with their crystalline counterparts published in [2, 3].

The bistable partner of the  $E'_\delta$ , the  $E'_\gamma$  center (see Fig. 1), is confirmed by a long range of theoretical studies [2, 6, 3]. One part of this configuration simply persists as a normal Si dangling bond carrying only one electron. The other part undergoes puckering, that is, the Si atom binds to a back O to stabilize this configuration. In the neutral charge state, the additional electron occupies the Si dangling bond.

In the hydrogenated variant of the O-vacancy (also termed H bridge), one H atom is located directly in-between both Si atoms, moving them apart. As illustrated in Fig. 3, this defect shows a strong asymmetry ( $d_{1,\text{Si-Si}} = 1.5$  Å and  $d_{2,\text{Si-Si}} = 12.2 - 2.8$  Å) with the H being attached closer to one of the Si atoms in the neutral case. For the positively charged Si atom, this asymmetry ( $d_{\text{Si-H}} = 1.6 - 1.8$  Å) nearly vanishes, which is in agreement with investigations in c-SiO<sub>2</sub> [2].

Interstitial atomic H was introduced by [2] to be a candidate for trapping in a-SiO<sub>2</sub>. In

the absence of any other type of defect, its bonding configurations are well established and can be explained in terms of electronegativity. Due to the polarity of the Si-O bond, more charge is distributed near the O atom. The proton is therefore attracted to the nearest network O atom with a bond length of 1.00 Å, where the negatively charged H is attached to a Si network atom with a bond length of 1.48 – 1.52 Å. Both values are in good agreement with values obtained in c-SiO<sub>2</sub> [2, 7]. In the neutral charge state, the H atom prefers a position in the middle of a void.

Now we address the defect levels for tunneling in and tunneling out of the defects, which are summarized in Tab. 1 and illustrated in Fig. 3. For the positively charged E'<sub>δ</sub> center, the energy level for neutralization is located 1.7 – 3.6 eV above the Si oxide valence band maximum. When an electron is allowed to tunnel into the trap, its energy level shifts down to the valence band of a-SiO<sub>2</sub>. As a consequence, the electron does not find a hole in the Si to escape the defect. Therefore, this trap remains neutral and is annealed permanently. This result is similar to the trap level behavior observed in c-SiO<sub>2</sub> [2]. In some cases, the trap level for tunneling in of an electron is found in the silicon bandgap. In consequence, this defect can also act as a fixed positive charge, if a hole is provided in the a-SiO<sub>2</sub> valence band.

As opposed to the E'<sub>δ</sub> center, the E'<sub>γ</sub> center has a trap level +/0 slightly above the Si conduction band minimum. The trap level after relaxation allows hole capture from the Si valence band. As far as the energetics of hydrogenated E'<sub>δ</sub> are concerned, the trap levels are located near the Si band edges so that this defect strongly interacts with the Si. Except for the case of charging the defect negatively, the H atom exhibits trap levels far from the Si band edges so that an exchange of electrons with the interface will not occur in a relevant extent.

## 4 Conclusion

We presented defect levels for tunneling in and tunneling out of a trap for several well-known defects and mimicked the oxide by a-SiO<sub>2</sub>. The E'<sub>δ</sub> center turned out to show a different behavior depending on the exact position of the transition energy ε<sub>0/+</sub>. The E'<sub>γ</sub> center as well as the H bridge is found to easily exchange electrons with silicon. In contrast, the H atom is revealed not to interact with the interface.

## 5 Acknowledgments

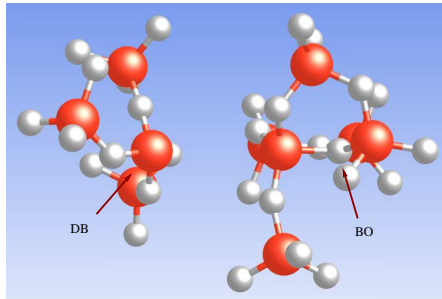
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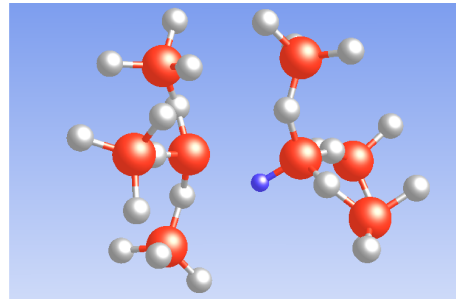
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	$E'_\delta$	$E'_\gamma$	$E'_\delta\text{H}$	H
+ / 0	1.7 – 3.6 eV	3.9 – 4.1 eV	4.4 – 4.9 eV	4.9 – 5.1 eV
0 / +	0.3 – 0.5 eV	2.1 – 2.4 eV	1.7 – 2.3 eV	0.3 – 0.9 eV
0 / -			4.1 – 4.3 eV	3.2 – 4.4 eV
- / 0			1.2 – 2.6 eV	0.9 – 1.2 eV

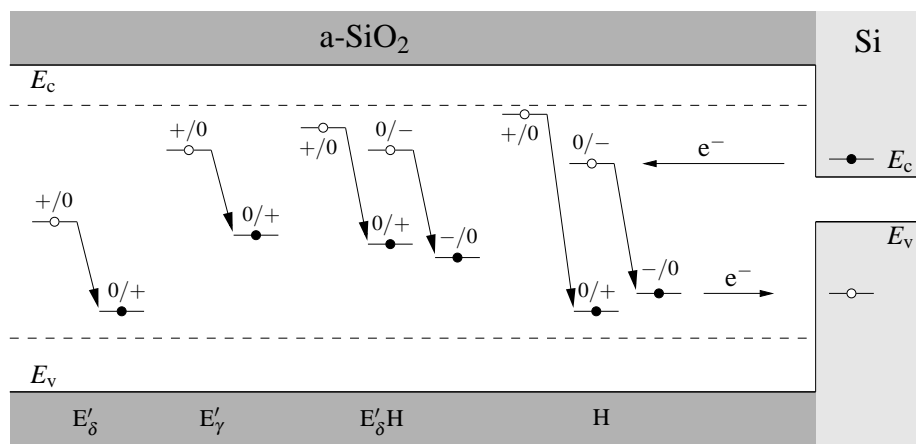
**Table 1:** Energy trap levels (+/0, 0/+, etc.) relative to the theoretical oxide valence band maximum of a-SiO<sub>2</sub>. The first sign denotes the equilibrium configuration of the defect in the corresponding charge state. The second sign gives the charge state of the defect for a given configuration.



**Figure 1:** Atomic structure of an  $E'_\gamma$  center. DB: dangling bond, BO: back O, red spheres: Si atoms, white spheres: O atoms



**Figure 2:** Atomic structure of a neutral hydrogenated  $E'_\delta$  center. This representation clearly demonstrates the asymmetry of the H bridge.



**Figure 3:** Band scheme including the calculated trap levels. The filled circles denote occupied defect levels, whereas open circles are unoccupied defect levels.