



# Dielectric breakdown in SiO<sub>2</sub> via electric field induced attached hydrogen defects

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## Abstract

We propose a new mechanism for dielectric breakdown in thin gate oxides. Using First Principles calculations, we have found a new meta-stable structure where an interstitial Hydrogen Radical attaches to a network Oxygen without breaking the Si-O bond (Att\_Rad state). Calculations in an external electric field find that the energy of the Att\_Rad state is reduced. A pair of such Att\_Rad states is further stabilized when they form a dimer (Att-Dimer state). This electric field induced Att-Dimer state is thermally accessible for very thin oxides and can form a percolating path that may explain the phenomenon of soft breakdown.

*Keywords:* thin gate oxide; dielectric breakdown; Hydrogen defects; electric field; First Principles calculation

## 1. Introduction

As MOSFET devices become smaller, the occurrence of Time Dependent Dielectric Breakdown (TDDB) in thin gate oxide increases substantially. In addition, a new mode of TDDB called soft breakdown appears as a precursor to hard breakdown. Soft breakdown is characterized by an excessive leakage current that is approximately reversible. Hard breakdown is irreversible.

TDDB is assumed to be due to the degradation resulting from the percolation of defects [1]. These defects arise from high-energy carrier fluxes [2,3],

external electric fields [4], or pre-existing defects related to Hydrogen [5]. The detailed nature of these defects is currently not well known. The number of pre-existing defects, believed to be Si-Si bonds in oxides, decreases for layer thickness smaller than about 10nm [6].

The operational electric field across a dielectric increases as the thickness decreases because the voltage necessary to operate the FET does not scale with dielectric thickness. With larger electric fields, Si-Si bond breakage may be induced. However, it is not large enough to induce Si-O bond breakage [4].

Using ab-initio Density Functional computations, we find a stable structure in SiO<sub>2</sub> in which interstitial Hydrogen attaches to O and stretches the nearby Si-O bonds (Attached-Radical state). This state is approximately 1.0 eV higher than the configuration where H resides in the interstitial region. The Attached-Radical state is thermally inaccessible at room temperature and is not considered relevant to dielectric breakdown.

By performing calculations on two-dimensional SiO<sub>2</sub> slabs in operationally realistic electric fields for thin dielectrics (on the order of 10 MV/cm), we find that the energy difference of the attached and interstitial H radical states are reduced (the diffuse electronic orbital connecting H to O in the attached radical is highly polarizable). A pair of such attached radical states is stabilized by an additional 1.4 eV when the O attached to the H atoms are both attached to the same Si (Attached-Dimer state) to form a spin singlet state.

Such electric field induced attached-dimer states can form percolating pathways through SiO<sub>2</sub> leading to breakdown. This electric field induced attached-dimer state is thermally accessible for very thin dielectrics and provides a mechanism that may explain the dielectric breakdown in thin oxides. The Attached-Dimer state can reversibly regenerate the pristine oxide plus an H<sub>2</sub> molecule when the applied voltage is removed, explaining the reversibility observed in soft breakdown.

## 2. Computational Method

First principles electronic structure calculations were carried out using SeqQuest, an efficient code developed at Sandia Labs for periodic density functional Theory (DFT) calculations using Pseudo potentials and Gaussian basis sets [7]. All described calculations used a Double-Zeta plus Polarization basis set and the Perdew-Becke-Ernzerhof (PBE) functional. Geometry optimizations of a single H in a 24(SiO<sub>2</sub>) three-dimensional supercell were performed with and without spin polarization, starting with the bulk quartz structure. Convergence with respect to total energy and rms force is less than 0.1 eV and 0.1 eV/Å, respectively. In addition, we performed two-dimensional slab calculations with the same number of SiO<sub>2</sub> molecules to determine the effect of real electric fields. An external electric field was applied to the two dimensional Si-SiO<sub>2</sub>-Si slab.

All calculations used a single k-point at Gamma, which is usually sufficient for an insulator with a large supercell.

The external electric field used is not the same as the experimentally measured applied field. The latter is the external field used in the calculation divided by the dielectric constant of SiO<sub>2</sub> ( $\epsilon$  is approximately 3.9). The dielectric constant can be obtained by calculating the voltage difference across the SiO<sub>2</sub>. We find the value to be consistent with experiments (3.5 to 4), serving as a further check on the accuracy of our electric field results.

## 3. Results and Discussions

The interstitial H (interstitial-radical) is known theoretically to be the most stable site for a neutral Hydrogen atom in  $\alpha$ -cristobalite [8] and is 1.8 Angstroms from the closest Oxygen (a normal OH bond is 1.0 Å).

To discover the structure of the new attached-radical state we used the following procedure. The positions of all atoms in the cell were geometry optimized for initial O-H distances varying from 0.9 to 2.1 Angstroms. If the starting crystal structure maintains its symmetry, then the H always converges back to the well-known interstitial H radical with an O-H separation of 1.8 Å.

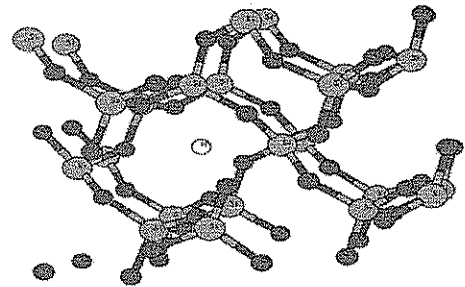


Fig.1 The Interstitial Radical state. The O-H distance is 1.8 Angstrom.

If we start by stretching the local Si-O bonds about 0.1 Angstroms, then for starting O-H distances less than 1.4 Å, the converged geometry always led to an O-H distance of 1.1 Å with two adjacent stretched Si-O bonds without breakage. We denote this locally

stable state as the attached-radical (Att\_Rad) structure. Figure 1 shows the interstitial-radical (Int\_Rad) structure and figure 2 is the attached-radical structure.

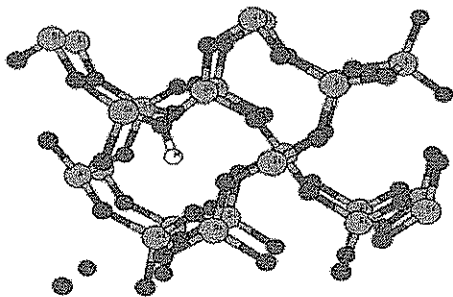


Fig.2 The Attached Radical state. The O-H bond distance is 1.1 Angstrom.

The Att\_Rad is 1.0 eV higher than the Int\_Rad state. The Att\_Rad would be further stabilized if the initial Si-O bond were elongated as occurs in realistic amorphous SiO<sub>2</sub>, but it is hard to imagine this state will be thermally accessible under normal operating conditions.

As the Att\_Rad state has a diffuse occupied electronic orbital, its energy will be sensitive to the magnitude of the applied electric field. Fig.3 shows that the Att\_Rad state becomes more stable than Int\_Rad in internal fields larger than 10MV/cm=1 V/nm. This value is of the order of the observed intrinsic breakdown field strength.

Two Att\_Rad states can be further stabilized by forming a spin singlet dimer (Att-Dimer). Figure 4 shows the optimized Att-Dimer state. This state is 1.4eV lower in energy in zero electric field compared to the energy of two separate Att-Rad states.

Att\_Dimer formation in applied electric fields leads to a new mechanism for TDDDB. This mechanism does not require pre-existing defects. Figure 5 shows the energy of the Att-Dimer as a function of the external electric field. With voltages across the dielectric leading to fields of approximately 5MV/cm, it is energetically favorable

for two Int\_Rad hydrogen atoms to form an Att\_Dimer state.

The above results are all derived using the quartz structure. The structure of the oxide near the Si-SiO<sub>2</sub> interface will naturally be more distorted than in quartz, with defects that make it easier to stabilize the Att-Rad and Att-Dimer states. Our estimates for these states in quartz represent an upper bound. Thus, we expect the electric fields necessary to create the attached H states in gate oxides may be substantially lower.

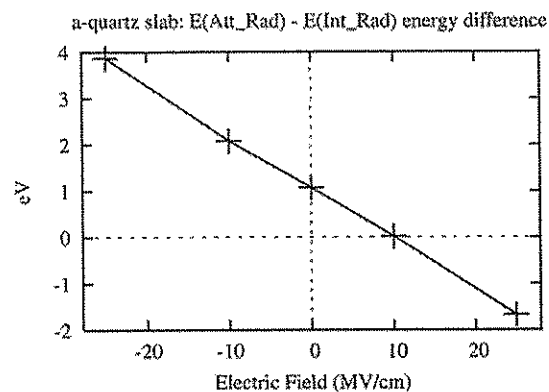


Fig.3 Energy Difference between the Att\_Rad state and the Int\_Rad state as a function of external electric field. The field is along the O-H bond.

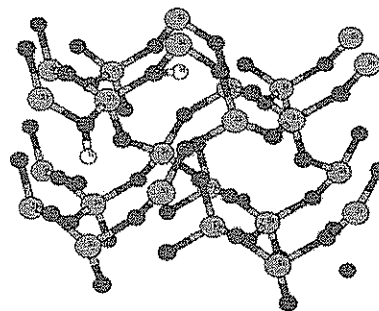


Fig.4 The Attached-Dimer state the O-H bond distance is 1.1 Angstrom.

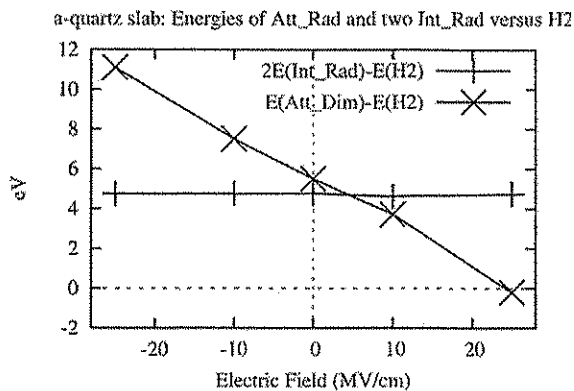


Fig.5 Energy Difference between two Int\_Rad hydrogen versus H<sub>2</sub>, and the Att\_Dimer and H<sub>2</sub>. At 5 MV/cm interstitial hydrogen will combine to form attached dimers. The field is along the O-H bond.

The population of Att\_Dimers is expected to be small in the bulk oxide. However, at the Si-SiO<sub>2</sub> interface, there are dangling bonds and passivated Si-H structures. This may lead to H<sub>2</sub> cracking, and also may be the source of Hydrogen radicals at the interface. The hot carriers at the anode may play an important role in generating H radicals by impact ionization. It is known that H radicals are unstable in SiO<sub>2</sub> and Si/SiO<sub>2</sub> interfaces [8,9]. Further analysis is necessary to understand this issue.

With our picture, soft breakdown for thinner oxides arises because the electric field is increased making the Att\_Dimer state more favorable. In addition, the interface, with its strained bonds, becomes a larger volume fraction of the oxide contributing to dimer formation. When the electric field is switched off, the attached H states will revert back to interstitial-radical states. This can explain the approximate observed reversibility in soft breakdown.

Joule heating from electron transport due to hopping along a percolating dimer pathway can lead to Si-O bond breaking and hard breakdown.

#### 4. Conclusions

Based on the above computations, we propose that soft breakdown in thin dielectrics arises from the attached H dimer states stabilized by applied electric fields. These states have diffuse “bond” orbitals and

lead to states in the bandgap. Percolation of H dimers leads to a pathway for electronic transport through the dielectric and eventual breakdown. The approximate reversibility of soft-breakdown is explained by H dimers reverting back to interstitial H and H<sub>2</sub> when the electric field is removed.

These considerations imply that control of Hydrogen at the interface is crucial to reduce TDDB for very thin oxides.

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