Atomistic Simulation of Defect Processes Involved in the Reaction-Diffusion-Drift Model of NBTI

Teofilo Cobos Freire
Department of Physics and Astronomy
UCL, London, UK
teofilo.freire.19@ucl.ac.uk

Souvik Mahapatra
Department of Electrical Engineering
IIT Bombay, Mumbai, India
souvik@ee.iitb.ac.in

Alexander L. Shluger
Department of Physics and Astronomy
UCL, London, UK
a.shluger@ucl.ac.uk

Abstract — **Density functional theory (DFT) simulations are used to model hole trapping reactions at hydrogen-containing defects in the bulk of amorphous SiO$_2$ (a-SiO$_2$) in the context of the reaction diffusion drift (RDD) model of NBTI. We report hole trapping, proton dynamics, and hydrogen release mechanisms related to bulk trap generation in the presence of hot holes, involving oxygen vacancies passivated by hydrogen (H$_2$-V$_O$) and water (H$_2$O-V$_O$). The charge transition levels (CTLs) and reaction barriers of these defect processes were calculated to predict their behavior under varying Fermi levels in metal-oxide-semiconductor field-effect transistors (MOSFETs) providing new insights into how these defects evolve during NBTI stress.**

Keywords— DFT calculations; Defect reactions, NBTI, Amorphous SiO$_2$

I. INTRODUCTION

The generation of traps due to breakage of chemical bonds at or near the channel/gate insulator interface and inside the gate insulator bulk of a MOSFET is responsible for drain current related parametric drift during Bias Temperature Instability (BTI) and Hot Carrier Degradation (HCD) stress [1, 2]. The same traps may also contribute to the increase in gate current during Stress-Induced Leakage Current (SILC) experiments and to Time-Dependent Dielectric Breakdown (TDDB) [1]. Historically, various modeling approaches customized for a specific experiment have been used to explain the measured data. In an attempt to introduce a universal, experiment-agnostic physical mechanism, the Reaction Diffusion Drift (RDD) model was proposed as a generalized trap generation framework to explain a plethora of measured data for BTI, HCD, SILC, and TDDB experiments [1, 2]. In this universal but defect-agnostic model outlined in Fig. 1, an experiment-specific initial trigger breaks chemical bonds (X-H) described by the forward (reverse) reaction parameters K_{F1} (K_{R1}). The released hydrogen (H) atoms diffuse and react to break other chemical bonds (Y-H, Z-H/O) described by reaction parameters K_{F2} (K_{R2}), K_{F3} (K_{R3}) and release molecular (H$_2$) and ionic (H$_2^+$, OH$^-$) species that diffuse or drift away to sustain trap generation during stress. The interface

trap generation during BTI stress uses channel cold carrier tunnelling as the initial trigger (and Reaction-Diffusion (RD) model, which is a subset of the generic RDD model without ionic species) [1]. Bulk trap generation during BTI, SILC and TDDB experiments uses hot electrons injected from the cathode and/or hot holes injected from the anode (generated via impact ionization in the anode caused by injected electrons from the cathode) as the initial trigger in RDD model [1, 3, 4]. A combined energy-thermionic framework that involves channel hot carriers and lattice heating is used as the initial trigger in RDD model during HCD stress [2].

Although the RDD model shows consistency between 1-D deterministic standalone, 3-D deterministic Technology CAD (TCAD), and 3-D stochastic (Kinetic Monte Carlo) implementations, and explains a plethora of experimental results [1, 2], it lacks an atomistic understanding of the defect processes involved. Atomistic models of some of the H-related defects which can be responsible for RTN and BTI have been discussed in [5]. In this paper, we use Density Functional Theory (DFT) calculations to screen potential other candidate defects X and investigate the nature of X-H bonds that could be broken by hot holes in a-SiO$_2$ in p-FET. This approach may help to identify the precursor of bulk trap generation during Negative BTI (NBTI) experiments [5].
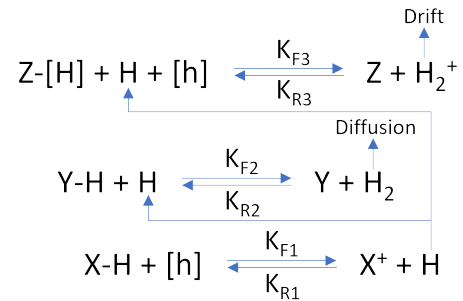

Fig. 1. Reaction diffusion drift framework for hole assisted hydrogen release.

II. SIMULATION METHODOLOGY

DFT calculations were performed on 30 different periodic models of bulk amorphous SiO$_2$, each containing 216 atoms, as detailed in [5]. The CP2K package [6] used for these calculations employs the Gaussian Plane Wave (GPW) method to

increase computational efficiency. The calculations employed the non-local hybrid functional, PBE0_TC_LRC [7], which is known to accurately reproduce the structure and band gap of SiO$_2$ [5]. The Goedecker-Teter-Hutter (GTH) pseudopotentials [8], combined with a double-ζ Gaussian basis set [9] and an energy cutoff of 650 Ry for the plane wave expansion of the electron density, were employed to represent silicon, oxygen, and hydrogen atoms. To facilitate efficient calculation of Hartree-Fock exchange contributions, an auxiliary pFIT3 basis set was utilized [10].

The energy barriers for proton diffusion were calculated using the climbing image nudged elastic band (CI-NEB) method with 7 replicas, implemented within the CP2K framework [6]. The charge transition levels (CTLs) for hole capture as a function of the Fermi level across the SiO$_2$ band gap were calculated as:

$$E_{form} = E_{def} - E_{bulk} - \Sigma\mu + q(E_{VBM} + E_F) + E_{corr}, \quad (1)$$

where E$_{def}$ is the total energy of the defective system, E$_{bulk}$ is the energy of the pristine a-SiO$_2$ structure and $\Sigma\mu$ is the sum of the chemical potentials. The chemical potentials for Hydrogen and Silicon were taken as the energies of hydrogen atom and single silicon atoms in bulk silicon, respectively. E_F is the Fermi energy of the system, and q is the charge state of the defect, E_{VBM} is the energy of the maximum of the valence band of the defect-free system and E$_{corr}$ is the correction term for the periodic interaction between localised charges in charged systems calculated using the method described in [11].

The offset of 4.5 eV was assumed for the Si/SiO$_2$ valence band maxima (VBM) based on an average value derived from spectroscopy experiments, which ranged from 4.3 to 4.7 eV [12-14] considering variations due to growth conditions and measurement techniques. The average band gap determined from 30 a-SiO$_2$ structures is 8.6 eV, slightly underestimating the established value of 8.9 eV for a-SiO$_2$ [15].

III. REACTION MODELS

The passivation of defects with hydrogen has long been utilized in the fabrication of electronic devices, with annealing in the forming gas commonly employed to suppress electrically detrimental defects, such as P$_b$ centres and oxygen vacancies. A fundamental assumption of the RDD model concerning the bulk traps that contribute to parametric shift during NBTI is that the pre-existing defect X is electrically inactive prior to hole trapping, but becomes electrically active following hydrogen release. Some of the candidate H-containing defects that could meet these criteria are illustrated in Fig. 2. They include oxygen vacancies passivated by H$_2$ and H$_2$O (Fig. 2, panels a and b) denoted as H$_2$-V$_O$ and H$_2$O-V$_O$, respectively. Other previously studied defects, the Hydrogen bridge (HB) [19] and Hydroxyl E' centre [20] are depicted in Fig. 2, panels c and d, respectively.

In this paper, we focus first on the less studied H$_2$-V$_O$ and H$_2$O-V$_O$ defects. The trapping of holes in these defects can result in the formation of a neutral 3-coordinated Si atom with an unpaired electron and the H$^+$ ion serving as the primary
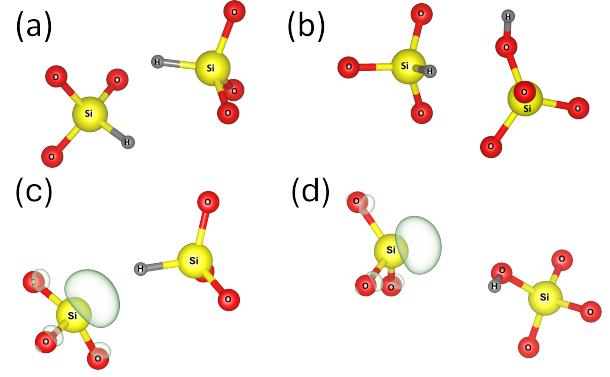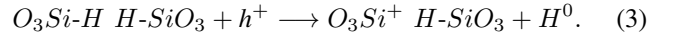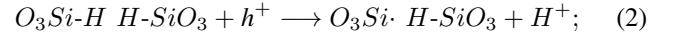

Fig. 2. DFT optimized atomic structures of hydrogen passivated defects and reaction products. (a) The H$_2$-V$_O$ defect. (b) The H$_2$O-V$_O$ defect. (c) The hydrogen bridge (HB) defect. (d) The hydroxyl E' centre. Green shaded areas represent the distribution of the unpaired electron in the defect.

positive charge carrier (eq. 2), or a positively charged defect and a neutral H atom (eq. 3):

$$O_3Si\text{-}H \; H\text{-}SiO_3 + h^+ \longrightarrow O_3Si\cdot \; H\text{-}SiO_3 + H^+; \quad (2)$$

$$O_3Si\text{-}H \; H\text{-}SiO_3 + h^+ \longrightarrow O_3Si^+ \; H\text{-}SiO_3 + H^0. \quad (3)$$

Our calculations demonstrate that reaction (eq. 2) leads to a thermodynamically more stable configuration with the formation of a proton, which is on average 0.9 eV lower in energy compared to eq. 3. This result is consistent with previous studies [5,17]. It suggests that created protons should capture electrons injected from the gate during bias application, in order to produce neutral hydrogen atoms and eventually H$_2$ molecules.

Let us consider more details of hole trapping reactions at H$_2$-V$_O$ and H$_2$O-V$_O$ defects in amorphous SiO$_2$, which have not yet been reported. We assume that these defects can be generated by reactions of H$_2$ and H$_2$O with neutral oxygen vacancies during film growth or anneal, followed by relaxation of the structure of the system. To simulate spontaneous hole injection, an electron is removed from the periodic cell, and its geometry is re-optimized introducing further structural distortions, allowing the hole to reside in the most thermodynamically favorable configuration.

In the case of H$_2$-V$_O$, upon hole trapping in all 30 structures considered, three distinct reactions were observed. The most common reaction involves the rotation of Si-H bonds, leading to a positive charge being shared between the two H atoms in 22 out of 30 structures (Fig. 3c), with an average inter-hydrogen distance of approximately 1.0 Å. In three structures, a spontaneous release of H$^+$ occurs, facilitated by proximity to neighboring O atoms (Fig. 3a,b) and small ring size, allowing diffusion of the proton without the energy barrier. In five structures, self-trapped holes were formed on wide-angle Si-O-Si bonds (Fig. 3d), consistent with previous reports [18]. These are excluded from the study because of their instability at room temperature.

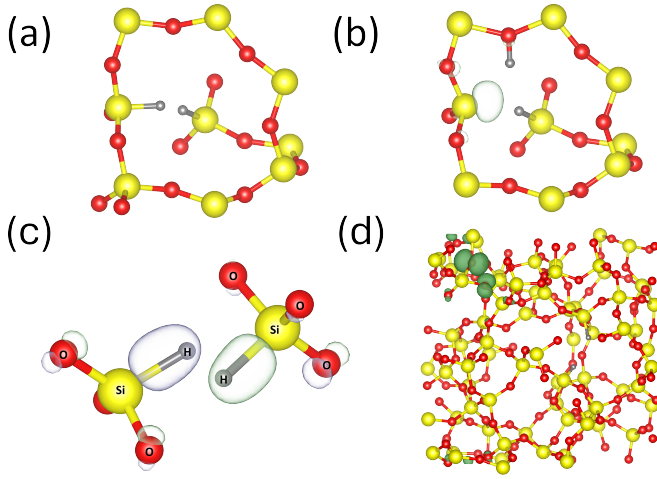The distribution of activation barriers for H$^+$ dissociation from H$_2$-V$_O$ defect in 22 amorphous SiO$_2$ structures is shown

Fig. 3. Atomic structures of H_2-V_O defect before and after hole trapping. (a) before hole trapping; (b) spontaneous H^+ release after hole trapping; (c) H_2-V_O^+ defect with hole localised between two hydrogens; (d) the self-trapped hole (STH) – the green spin density in a-SiO_2.

in Fig. 4. The average dissociation barrier is 1.1 eV, with values ranging between 0.5 eV and 1.4 eV. The relatively high average barrier is attributed to breaking the strong H-H bond, which is required to initiate the proton migration. Following the proton release, the system transforms into the HB center and H^+, a defect that have been extensively investigated both experimentally and theoretically [5,19].
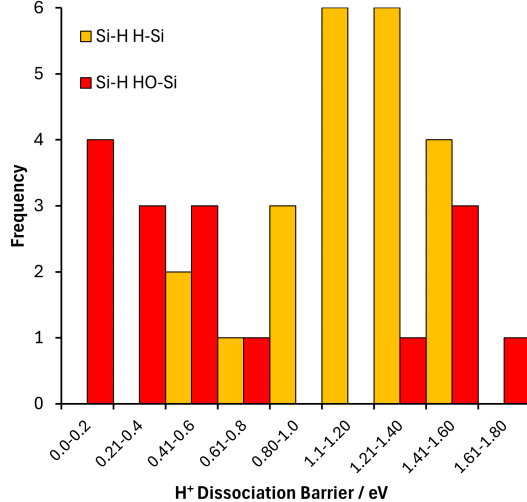

Fig. 4. H^+ dissociation barriers for H_2-V_O (yellow) and H_2O-V_O (red) in a-SiO_2.

In the case of the H_2O-V_O defect, the spontaneous hole trapping on a defect was observed only in 17 of 30 structures, and the hole polaron formation identified in 5 structures. In the remaining 8 structures, a spontaneous release of either a proton or a neutral hydrogen (Fig. 5b) occurred, driven by the recombination of the Si-O bond from Si-H and O-H groups and redistribution of the positive charge. The most probable mechanism involves the spontaneous jump of H^+

to the -OH group, forming H_2O^+ (Fig. 5a), with an average H^+ dissociation barrier of 0.6 eV, ranging from 0.1 eV to 1.7 eV. Low dissociation barriers were observed when proton dissociation occurred across Si-O-Si rings, while higher barriers were associated with dissociation to the nearest O atom within the same Si tetrahedron, as shown in Fig. 6. Upon the hydrogen release, the resulting defect is a three-coordinated Si atom with an unpaired electron adjacent to a Hydroxyl group, also known as the HE center (Fig. 2(d)) [20]. This defect can also form when an H^0 atom reacts with strained (>1.65 Å) Si–O bonds in a-SiO_2 [21].
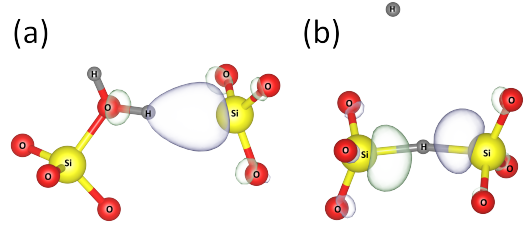

Fig. 5. Atomic representation of hole trapping on H_2O-V_O defect. (a) Lowest energy configuration with H^+ on OH group and (b) H^0 producing structure with hole distributed on H^+ between two Si.
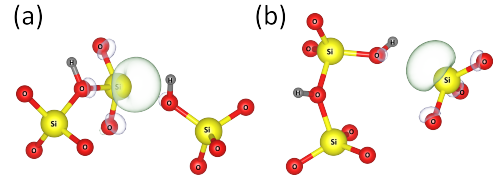

Fig. 6. Optimized atomic structures of H^+ diffusion for hole trapped H_2O-V_O defects. (a) H^+ diffusion across ring and (b) H^+ diffusion to the same Si tetrahedron bearing the -OH group.

The thermodynamically favorable charge state of a defect is determined by the relative position of its charge transition level to the Fermi level. When a defect captures a charge, the localization of the electron within the oxide disrupts the electrostatic equilibrium of the device, causing threshold voltage shifts. The application of a gate bias in a MOS device alters the trap level position because of the bending of the band near the interface and the resulting electric field within the oxide. When the Fermi level is below the CTL, the defect remains in a positive charge state, whereas above the CTL, the neutral state is favored. At the CTL, the two charge states become equally stable.

The hole trapping (+1/0) CTLs for the H_2-V_O and H_2O-V_O defects in a-SiO_2, relative to the Si Fermi level, are shown schematically in Fig. 7 in a rigid band approximation. The average hole transition level for H_2-V_O (+1/0) is 0.9 eV relative to the top of the a-SiO_2 valence band, with a range of 0.3 eV to 1.3 eV. In contrast, the transition level for the H_2O-V_O defect averages 1.5 eV above the a-SiO_2 valence band, with a range of 1.2 eV to 2.1 eV. In p-type MOSFETs, the probability of cold hole capture from the Si valence band into these hydrogen-passivated defects is therefore expected to be low due to a significant heat dissipation required in this
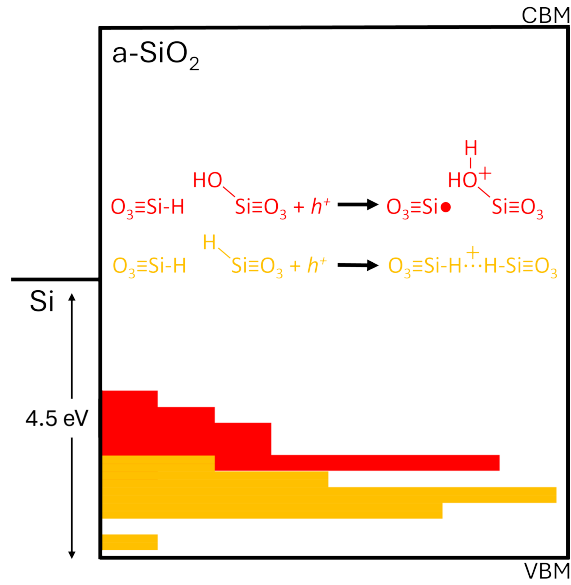
Fig. 7. Si/SiO$_2$ band diagram with hole trapping (0/+1) distributions for Oxygen vacancies passivated by H$_2$ (yellow) and H$_2$O (red).

process. The tunneling of hot holes could, however, facilitate these reactions.

Hot hole injection has long been considered to be responsible for trap generation during SILC/TDDB experiments [1, 3, 4, 22]. In the Anode Hole Injection (AHI) process, when a high electric field is applied across SiO$_2$, substantial band bending enables electrons to tunnel through the a-SiO$_2$ conduction band, gaining kinetic energy as they accelerate. These high-energy electrons generate electron-hole pairs via impact ionization in the anode. The resulting hot holes can tunnel and become trapped in defect states near the edge of the a-SiO$_2$ valence band, in this case the defect levels of H$_2$ and H$_2$O-V$_O$. The released hydrogen atoms then can diffuse and create further defects. This work (along with [4]) can help to reconcile the debate about AHI versus AHR (Anode Hydrogen Release) related to SILC/TDDB [22, 23]. This requires providing cross sections and rates for hot hole trapping and Si-H bond breaking in these reactions, which still remain challenging [24].

IV. CONCLUSIONS

We used density functional theory to explore hydrogen-related defect processes in amorphous SiO$_2$ within the Reaction Diffusion Drift (RDD) model for bulk trap generation during NBTI, focusing on the behavior of hydrogen-passivated oxygen vacancies, as well as the mechanisms of hole trapping, proton and hydrogen release. Further research is necessary to examine other defect types associated with RDD model, which may yield deeper insights into degradation in microelectronic devices during BTI, SILC/TDDB and HCD experiments.

REFERENCES

[1] S. Mahapatra, "A Generic trap generation framework for MOSFET reliability—part I: gate only stress–BTI, SILC, and TDDB," IEEE Transactions on Electron Devices, vol. 71, pp. 114–125, Jan 2024.

[2] S. Mahapatra, "A Generic trap generation framework for MOSFET reliability—part II: Gate and Drain Stress—HCD," IEEE Trans. Electron Dev., vol. 71, pp. 126–137, Jan 2024.

[3] D. Saha, D. Varghese and S. Mahapatra, "Role of anode hole injection and valence band hole tunneling on interface trap generation during hot carrier injection stress," in IEEE Trans. Electron Dev., vol. 27, no. 7, pp. 585–587, Jul 2006.

[4] T. Samadder and S. Mahapatra, "Tunneling Leakage Current Dependent RDD Model Framework for Gate Oxide TDDB,"in Proc. Int. Conf. Simulation Semiconductor Processes and Devices, Kobe, Japan, pp. 193-196, Sep 2023.

[5] Y. Wimmer, A-M. El-Sayed, W. Gös, T. Grasser and A. L. Shluger "Role of hydrogen in volatile behaviour of defects in SiO$_2$-based electronic devices" Proc. R. Soc. A, vol. 472, pp. 2190, Jun 2016.

[6] J. Hutter, "CP2K: An electronic structure and molecular dynamics software package - Quickstep: Efficient and accurate electronic structure calculations" J. Chem. Phys., vol. 152, pp. 194103, May 2020.

[7] M. Guidon, "Robust Periodic Hartree–Fock Exchange for Large–Scale Simulations Using Gaussian Basis Sets"J. Chem. Theory Comput., vol. 5, pp. 3010–3021, Nov 2009.

[8] S. Goedecker, M. Teter and J. Hutter, "Separable dual-space Gaussian pseudopotentials" Phys. Rev. B., vol. 54, pp. 1703–1710, Jul 1996.

[9] J. VandeVondele and J. Hutter, "Gaussian basis sets for accurate calculations on molecular systems in gas and condensed phases" J. Chem. Phys., vol. 127, pp. 114105, Sep 2007.

[10] M. Guidon, J. Hutter and J. VandeVondele, "Auxiliary Density Matrix Methods for Hartree–Fock Exchange Calculations" J. Chem. Theory Comput., vol. 6, pp. 2348–2364, Jul 2010.

[11] S. Lany and A. Zunger, "Accurate prediction of defect properties in density functional supercell calculations" Modelling Simul. Mater. Sci. Eng., vol. 17, pp. 084002, Nov 2009.

[12] E. Vescovo, "Band offsets of ultrathin high-κ oxide films with Si" Phys. Rev. B, vol. 78, pp. 085114, Aug 2008.

[13] A. C. Diebold, "Complete band offset characterization of the HfO$_2$/SiO$_2$/Si stack using charge corrected x-ray photoelectron spectroscopy" J. Appl. Phys., vol. 107, pp. 043702, Feb 2010.

[14] R. J. Nemanich, "Measurement of the band offsets of SiO$_2$ on clean n- and p-type GaN(0001)" J. Appl. Phys., vol. 93, pp. 3995–4004, Apr 2003.

[15] A. J. Garza and G. E. Scuseria "Predicting Band Gaps with Hybrid Density Functionals" J. Phys. Chem. Lett., vol. 7, pp. 4165–4170, Oct 2016.

[16] S. Ling, A-M El-Sayed, F. Lopez-Gejo, M. B. Watkins, V.V. Afanas'ev and A. L. Shluger, "A computational study of Si–H bonds as precursors for neutral E' centres in amorphous silica and at the Si/SiO$_2$ interface" Microelectronic Engineering, vol. 109, pp. 310-313, Sep 2013.

[17] V. V. Afanas'ev and A. Stesmans, "Proton nature of radiation-induced positive charge in SiO$_2$ layers on Si" EPL, vol. 53, pp. 233, Jan 2001.

[18] D. L. Griscom, "Self-trapped holes in amorphous silicon dioxide" Phys. Rev. B, vol. 40, pp. 4224–4227, Aug 1989.

[19] P. E. Blochl, "First-principles calculations of defects in oxygen-deficient silica exposed to hydrogen" Phys. Rev. B, vol. 62, pp. 6158–6179, Sep 2000.

[20] A-M El-Sayed, M. B. Watkins, T. Grasser, V. V. Afanas'ev, and A. L. Shluger, "Hydrogen–induced rupture of strained Si-O bonds in amorphous silicon dioxide" Phys. Rev. Lett., vol. 114, pp. 115503–115508, Mar 2015.

[21] A-M. El-Sayed, Y. Wimmer, W. Goes, T. Grasser, V. V. Afanas'ev and A. L. Shluger."Theoretical models of hydrogen-induced defects in amorphous silicon dioxide" Phys. Rev. B, vol. 92, pp. 014107, Jul 2015.

[22] M. A. Alam, J. Bude and A. Ghetti, "Field acceleration for oxide breakdown-can an accurate anode hole injection model resolve the E vs. 1/E controversy?," IEEE Int. Reliab. Phys. Symp. Proc., San Jose, CA, USA, 2000, pp. 21-26.

[23] J. H. Stathis, "Physical and predictive models of ultrathin oxide reliability in CMOS devices and circuits," in IEEE Trans. Device Mater. Rel., vol. 1, pp. 43-59, Mar 2001.

[24] M. Jech, A-M. El-Sayed, S. Tyaginov, A. L. Shluger, and T. Grasser, "Ab initio treatment of silicon-hydrogen bond rupture at Si/SiO2 interfaces," Phys. Rev. B vol. 100, pp. 195302 2019