



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 871813.

ICT Project No 871813 MUNDFAB

Modeling Unconventional Nanoscaled Device FABrication

D5.5: Final atomistic catalog of chemical reactions relevant for defect formation

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17.02.2023



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Abstract

In this deliverable we use ab-initio methods like density functional theory (DFT) to study the microscopic mechanisms involved in important process steps like thermal Si oxidation and to also analyze the properties in atomistic defects in technologically relevant materials like amorphous SiO₂, Si₃N₄, or Si_xGe_{1-x}O₂. These findings are particularly important for developing new reliability models for nanoelectronic devices within the scope of WP6.

1 Thermal Oxidation of Si

Despite its technological importance for nanoelectronic devices, microscopic details of the thermal Si oxidation process are still elusive. For example, the mechanism causing an amorphization of the growing oxide had been unknown until recently [1]. Here we employ a multiscale atomistic modeling approach to study the various reactions occuring at the Si/SiO₂ interface over several timescales as depicted in Fig. 1. Building on the previous work presented in D5.2, we perform molecular dynamics (MD) simulations within density functional theory (DFT), density functional based tight-binding (DFTB) and a machine-learned force field to shed some light on the intricacies of the oxidation process.



Figure 1: Various stages of the Si oxidation process. During the initial stage, a direct dissociation of O_2 at the Si surface is triggered by a charge transfer (left). After saturating the surface with O, further oxidation slows down and proceeds via so-called molecular precursors (middle). Lastly, O_2 molecules diffuse through the now inert SiO₂ layer and dissociate at the Si/SiO₂ interface (right). Reprinted from [1].

1.1 O2 Dissociation at the Si Surface

We start our investigation with the adsorption and subsequent dissociation of an O₂ molecule at the pristine Si surface. The technologically relevant Si(100) surface exhibits a p(2x2) surface reconstruction at temperatures above 950°C [2], which was hence chosen as a starting point for the atomistic simulations. In order to simulate the initial stage of the oxidation, we performed ab-initio molecular dynamics simulations on a 4x4x12 Si slab with a single O₂ molecule placed 2.5Å above the reconstructed surface. After assigning the initial atomic velocities in the slab according to a random sample of the Maxwell-Boltzmann distribution at T=1000K, the system was propagated for 3ps in a microcanonical (NVE) ensemble with a timestep of 0.5fs. This procedure was repeated several times with different initial conditions to gather consistent statistically significant results.

For most trajectories, the O_2 molecule approached the surface followed by a spontaneous dissociation and incorporation of O into the Si bond center sites of the surface dimers as shown



Figure 2: Snapshots of the charge transfer mediated spontaneous O_2 dissociation at the pristine Si(100) p(2x2) surface (top). The Mulliken charge analysis (bottom left) indicates a charge transfer from a Si surface dimer to the O_2 molecule, triggering the dissociation and subsequent incorporation of O in the Si bond center sites with an energy gain of over 7eV per molecule (bottom right). Reprinted from [1].

in Fig. 2. Closer inspection of the Mulliken charges [3] along the MD trajectories reveals the transfer of an electron from the Si dimer into the antibonding π^* orbital of the O₂ molecule. This is then followed by a spontaneous dissociation with an energy gain of over 7eV per molecule. Those findings are consistent with earlier theoretical investigations [4] as well as experimental STM images of a sparsely oxidized Si(100) surface [5].

1.2 Onset of Amorphization

Earlier theoretical studies were primarily focused on the crystalline Si/SiO₂ interface [6], while it is experimentally well established that the SiO₂ grown by oxidation is amorphous. This fact even holds true for very thin oxide layers between 10Å-50Å deposited with rapid thermal oxidation (RTO) [7]. Despite this evidence, it is still unclear at which stage of the oxidation the amorphization sets in. Earlier ab-initio investigations based on static calculations, i.e. geometry relaxations at 0K, suggested the existence of a crystalline oxide monolayer at the beginning of the oxidation process [6]. By overcoming the restrictions of static calculations, we show, however, that an amorphous interface forms immediately at the beginning of the oxidation.

In order to accurately model the physical oxidation process, we performed ab-initio MD simulations with the O_2 gas phase being mimicked by adding consecutive O_2 molecules into the simulation cell. In these calculations, the substrate slab was kept at 1000K, which is within the typical temperature range used experimentally to oxidize Si. The O_2 molecules were introduced with a velocity of 1000m/s in a random direction but with a component towards the surface. This was done to overcome the adsorption barrier forming at higher O coverage of the surface. However, considering the mean velocity of an O_2 molecule at 1000K being roughly 810m/s according to the Maxwell-Boltzmann distribution, such a velocity is well within reasonable physical bounds.

These simulations were performed multiple times with identical initial positions, but slightly different initial velocities drawn from the thermal Maxwell-Boltzmann distribution for the Si substrate. As shown in Fig. 3, the corresponding adsorption trajectories result in completely



Figure 3: Dynamical simulations of the first oxidation stages with slightly different initial velocities. As shown by these two trajectories, even small changes in the initial conditions result in completely different final configurations, suggesting an immediate amorphization of the forming oxide layer. Reprinted from [1].

different final configurations with comparable energy gains. This finding indicates an immediate amorphization already in the first stages of the oxidation process.

1.3 Molecular Precursors and Advancing Oxidation

In the stepwise oxidation process described above, we observe a transition from an initially spontaneous O₂ dissociation to a regime at higher surface coverage, where an adsorption barrier arises and hence the oxidation rate is slowed down. Since these processes happen on timescales longer than 1ps, their simulation using ab-initio methods quickly becomes infeasible. For this reason, we employ the much faster density functional based tight-binding (DFTB) method as implemented in the DFTB+ [8] software package to extend the feasible simulation time to several 10ps. Within DFTB, the self-consistent Kohn-Sham equations known in DFT are approximated by a tight-binding Hamiltonian derived from the Harris functional. This approach is typically 3 orders of magnitude more efficient than solving the Kohn-Sham system at the expense of requiring a semi-empirical Slater-Koster parametrization for the occurring overlap integrals. In this work we use the pbc-0-3 parameter set for the elements Si, O and H, which gives good agreement with DFT calculations for the Si/SiO₂ interfacial system [9].

Using DFTB for a similar stepwise procedure as described in section 1.2, we observe less and less spontaneous dissociation events as the O surface coverage increases and the first continuous oxide layer is forming. Instead, the O₂ molecules adsorb via a metastable molecular precursor as shown in Fig. 4. The adsorption and incorporation of additional O now requires a large relaxation of the surface as well as breaking and reforming of already existing Si-O bonds, which significantly reduces the reaction rates.



Figure 4: Molecular precursor states. The O_2 first adsorbs to an already fully oxidized Si atom for around 4ps before dissociation. During this process, 2 O atoms migrate into a sub-surface layer in order to make room for the additional O atoms. Reprinted from [1].

We continued these simulations until a 8.5Å thick oxide layer is formed. At this point, all Si atoms at the surface are fully oxidized, meaning they have 4 Si-O bonds, and the surface is separated from the bulk Si by a roughly 5Å thick transition layer, see Fig. 5 (left) and Fig. 6. Within this transition layer, the oxidation state of Si continuously changes from 0 (bulk Si) to



Figure 5: Characteristics of the SiO₂ growth obtained by dynamic simulations within DFTB. The atomistic structure exhibits a region of fully oxidized Si on the surface and a roughly 5Å thick transition layer towards the bulk Si (left). Even for such thin oxide layers, the bond length and angle distributions are already comparable to experimental values obtained for bulk SiO₂ [10]. Reprinted from [1]

+4 (bulk SiO₂), however the distribution of Si-O bond lengths and angles is already approaching experimental values for vitreous bulk silica [10] as shown in Fig. 5 (right).

In previous works, an amorphous Si/SiO₂ interface was typically obtained by a melt and quench procedure starting from an initially crystalline interface. In this technique, the structure is partially melted in a classical MD run and subsequently cooled down slowly to obtain an amorphous interface [11]. While this procedure is practical and can even provide defect-free structures, it is assumed to result in too idealistic interfaces due to the artificial melt-quench procedure, which does not resemble the actual physical growth process. A detailed comparison between a melt-quench created structure and an interface obtained by the new stepwise oxidation technique is shown in Fig. 6. Although the two structures have comparable transition regions, the stepwise structure clearly has a larger degree of disorder as is evident by the distorted Si-O bonds and Si-O-Si angles. These distortions indicate a considerable amount of strain at the interface consistent with experimental findings reporting a stress of 0.3 to 0.8 GPa at the interface [12].



Figure 6: Comparison between melt&quench and stepwise created Si/SiO₂ interfaces.(a) The stepwise structures have elongated bonds and distorted angles indicating mechanical stress at the interface. (b) The melt-quench method produced mostly two-fold O-coordinated Si reminiscent of crystalline interfaces. In contrast, the stepwise approach yields higher coordinated Si atoms. (c) Oxidation state of Si estimated by a Mulliken charge analysis as a function of the distance to the surface. (d) Histogram of the Si distribution along the z-axis. The stepwise structure again shows a broader distribution, indicating a larger amount of disorder. Reprinted from [1].



Figure 7: Diffusion of O_2 as observed in our ab-initio MD simulations. The molecule easily diffuses through the oxide and dissociates at the interface via a charge transfer reaction similar to the spontaneous dissociation at the clean surface. Reprinted from [1].

1.4 Diffusive Regime

In later stages of the Si oxidation, the surface as well as the already formed oxide become inert to further reactions with O_2 since all the Si in these regions is already fully oxidized. Here, the oxidation enters the well-known diffusive regime described by the famous Deal-Grove model [13]. In this regime, O_2 easily diffuses through the oxide with diffusion barriers of approximately 0.5eV [14]. We were able to reproduce this behavior in our simulations by using a large interface structure created with the melt-quench procedure and subsequent passivation of the SiO₂ surface with hydrogen. As shown in Fig. 7., a 3ps long ab-initio MD trajectory shows the seamless diffusion of a O_2 molecule towards the interface, where it dissociates upon charge transfer similar to the dissociation process described earlier for the clean Si surface.

Besides diffusion of O_2 , we also investigated other transport mechanisms like hopping of O atoms between Si bond center sites both in SiO₂ and bulk Si by applying the nudged elastic band (NEB) [15] method to find the minimal energy transition path. However, our studies show, that these competing mechanisms have much larger barriers (1.7-2.7eV) [1] compared to the O_2 diffusion. We hence conclude that O_2 diffusion is the dominant transport mechanism in this regime.

2 Defects in a-SiO₂

During the growth of amorphous SiO_2 (a- SiO_2), or any other dielectric for this matter, the formation of defects in unavoidable. In particular, hydrogen-related defects in a- SiO_2 have drawn a lot of attention recently as they are suspected to cause reliability issues like bias temperature instability (BTI) in MOSFET devices through charge trapping. While most experimental and theoretical investigations so far were focused on hole trapping during negative BTI (NBTI), electron trapping in a- SiO_2 received much less attention. Here we present



Figure 8: Verification of the a-SiO₂ model structures. The bond length and angle distributions (left) agree welll with X-ray and neutron diffraction measurements in [18]. The structure factor (right) is in excellent agreement with the results from neutron scattering experiments on a-SiO₂ thin films [19]. Reprinted from [21].

a detailed study on oxygen vacancy (OV), hydrogen bridge (HB) and hydroxyl-E' center defects in a-SiO₂ and show that they are generally amphoteric, meaning they can act as hole and electron traps simultaneously. Defect parameter distributions are obtained with DFT which allow to simulate the charge trapping behavior of the defects under arbitrary bias conditions. These parameter sets are crucial for describing charge trapping and device reliability at the TCAD level in WP6.

2.1 Structure Creation and Verification

In order to study defects in a-SiO₂, a suitable atomistic model of the amorphous host material is required. Here we employ the melt-quench technique to create sample structures of a-SiO₂ containing 216 atoms. A crystalline 3x3x3 supercell of β -cristobalite was melted at 5000K in the LAMMPS package [16] by using a classical ReaxFF-type forcefield parametrized for Si/SiO₂ interfaces [17]. This forcefield was chosen because of its ability to describe dynamical bond formation and breakage. Subsequently, the melt was quenched at a rate of 6K/ps with a stepsize of 0.1fs. The obtained structures were further relaxed in DFT with residual forces below 25meV/Å and mechanical stress below 0.01GPa. Note that the angles between the cell base vectors were also allowed to relax in order to remove any residual shear stress within the structures. This results in triclinic simulation cells with angles slightly deviating from 90°.

Due to the melt-quench procedure being intrinsically artificial and the use of an empirical forcefield to perform the MD simulations, the resulting amorphous structures need to be tested against available experimental data. Fig. 8 (left) shows the distribution of bond lengths and angles in the obtained structures, which are in good agreement with experimental data from high-energy X-ray and neutron diffraction measurements [18]. Furthermore, as depicted in Fig. 8 (right), the structure factor of our model structures is in excellent agreement with results from neutron scattering experiments on a-SiO₂ thin films [19]. Note that contrary to the previously discussed oxidation of Si, the idealistic structures obtained from melt-quench MDs are desirable here, in order to study individual defects which are introduced by hand starting from an perfectly coordinated a-SiO₂ structure.

In total, 20 amorphous structures were created. Among these, one representative structure was selected (its bond length and angle distribution is also depicted in Fig. 8 (left)) and 144 defects of each type (OV, HB and HE) were inserted at each O site of this structure. Each defect configuration is then relaxed within DFT in multiple charge states to obtain all possible states of the defect.

2.2 Defect Formation

One key quantity for a defect is its so-called formation energy. It determines the amount of energy required to create a single defect in a pristine host material. Hence, large formation rather low energies indicate а defect concentration and vice versa. The formation energies for the 3 defect types studied in this work are collected in Fig. 9. Although the OV is the canonical defect in a-SiO₂, it has large formation energies in the range of 5-8eV. This is consistent with experimental evidence indicating a low concentration of OV defects in a-SiO₂ [20]. Further note that there is a pronounced difference in formation energies for the puckered and unpuckered variants of the OV. Although the HB and HE defects also exhibit a possible puckering transition, for those defects, both configurations statistically have the same formation energy. The HB defect has a similar formation energy to the OV, which is not surprising, since the OV is its precursor, becoming an HB upon hydrogenation. Contrary, the HE center forms by an H atom breaking a strained Si-O bond and has a substantially lower formation energy of 2.45eV on average.



Figure 9: Formation energy statistics of the OV, HB and HE defects in their neutral charge states. Reprinted from [21].

Therefore, this defect is likely to occur in the presence of hydrogen and will be studied in more detail below. For details about the OV and HB defects we refer to [21].

2.3 The Hydroxyl-E' Center

Although defects in crystalline SiO_2 have been studied extensively both theoretically and experimentally, the existence of the HE center in a-SiO₂ was only confirmed rather recently with ab-initio methods [22]. The main reason for its late discovery is that its formation requires a strained Si-O bond, which is not present in crystalline SiO_2 polymorphs but only in amorphous silica. Such strained bonds preferably occur near the Si/SiO₂ interface, indicating that the HE center concentration will get larger towards the MOSFET channel and thus this defect likely plays an important role for device reliability.

While the HE center was thought to be primarily responsible for hole trapping during NBTI conditions [23], our investigation shows that it is in fact amphoteric and hence can also act as an electron trap. The neutral and positive charge states of the HE center have been studied previously [24], however, we additionally found a large number of different negatively charged HE configurations as depicted in Fig. 10 (left). Despite this apparent variety, all studied defects have a very similar minimal energy configuration in the negative charge state (f in Fig. 10 left) which is energetically more favorable by at least 1.5eV compared to the other states discovered. In this stable configuration, the H binds to an already fully coordinated Si, while the previously broken Si-O bond is restored. Furthermore, as demonstrated in Fig. 10 (right),



Figure 10: Left: Various different configurations of the HE center in multiple charge states. While there is a large variety of negatively charged states, all investigated defect sites showed an almost identical minimal energy configuration in the negative charge state (f). Right: Nudged elastic band calculations show that most other states are separated by only a small barrier to this minimum energy state. Reprinted from [21]

most of the other meta-stable negative states are connected to this stable minimum state by a very small barrier, indicating that when negatively charged, the defect will quickly relax into this preferred state.

For modeling the impact of defects on the device reliability, the atomistic details of a defect cannot be treated explicitly within a TCAD simulation. Instead, the charge trapping dynamic of the defect is described by a Markov chain as shown in Fig. 11 (left). Here, all the defect physics is encoded in the transition rates between the individual states. During a thermal transition (solid lines), the charge of the defect is conserved, while it undergoes a structural relaxation into a different state. This type of transition can be described within the classical transition state theory. However, there are also transitions, where the defect exchanges charges with the semiconductor substrate. These transitions are particularly important in the context of device reliability, since they allow the defect to trap charges and hence change the electrostatics of the device causing detrimental effects like BTI or random telegraph noise (RTN). Such a transition is described within the framework of nonradiative multiphonon (NMP) theory [24]. One key parameter in NMP theory is the thermodynamic trap level (CTL), which determines the preferred charge state at a given Fermi level. In order for a defect to trap/emit charges from/to the valence or conduction band of the semiconductor, the CTL has to be in the vicinity of the respective band edge. Fig. 11 (right) shows the CTLs for the HE center w.r.t. the Si band



Figure 11: 7-state diagram of the hydroxyl-E' center in $a-SiO_2$ (left). During charge transitions (dashed lines) the defect exchanges charges with the semiconductor valence or conduction band, whereas for thermal transitions (solid lines), the net charge of the defect is conserved. The distribution of thermodynamic charge transition levels (right) w.r.t. the band edges of the semiconductor determine the stability of the different charge states. Charge transitions are only possible for trap levels in the vicinity of the semiconductor band edges. Reprinted from [21]

edges. The meta-stable negative states (3') show CTLs near the conduction band edge of Si and would thus allow for efficient electron trapping. However, the CTL of the most stable negative charge state (3) lies well below the Si conduction band and therefore effectively suppresses dynamical electron trapping during device operation. This is consistent with the experimental observation that PBTI (electron trapping) is much less pronounced than NBTI (hole trapping) for standard Si devices [25]. This finding also suggests the HE center to cause BTI in these devices. The full set of parameters to describe each individual transition, as required for an implementation in a TCAD device model, can be found in [21].

3 Defects in Nitrided Oxides

Although SiO₂ is the native oxide of Si and hence has been the go-to dielectric in MOSFETs for decades, the continued downscaling of device dimensions made it necessary to use other dielectrics. One prominent example is the use of nitrided SiO₂ (SiON) to reduce the gate leakage currents as well as the diffusion of boron dopants through the oxide layer. In a first step towards understanding charge trapping in SiON, we study intrinsic charge traps (polarons) in amorphous Si₃N₄.

3.1 Structure Creation and Verification

Similar to SiO₂, a credible atomistic model of amorphous Si₃N₄ has to be established in order to study charge trapping in this material from first principles. However, while there are classical force fields available for Si₃N₄ [26], none of them were found to be suitable for a melt-quench MD to obtain an amorphous sample from the initially crystalline state. The use of these force fields lead to significant N₂ segregation and a large number of coordination defects in the resulting structures. Such defective structures are not only physically wrong but als make it impossible to study particular defects individually or trap charges at a particular defect site. In order to solve these problems, a modified Billeter potential [26] was used, where the attractive N-N interaction was removed to prevent the formation of N₂ molecules. With this potential and



Figure 12: Structural characterization of amorphous Si_3N_4 models. The radial distribution function (left) and the structure factor (right) are in good agreement with experimental neutron scattering and X-ray diffraction data respectively [35].



Figure 13: Electronic projected density of states for $a-Si_3N_4$. With no excess charge present, there are no states in the bandgap (left). However, when injecting holes (middle) or electrons (right), the excess charge self-traps and forms localized states in the bandgap. Note that, contrary to actual defects, these states are not present before the charge is introduced.

a MD profile similar to the SiO₂ case, credible Si₃N₄ structures with a low defect concentration and reasonable agreement with experimental structure factors were obtained, see Fig. 12. The bandgap of 4.5eV is also in good agreement with experimental values [27], as can be seen in Fig. 13 (left).

3.2 Intrinsic Charge Trapping

While defects are the prototypical charge trapping centers in oxides, recently a different electron trapping mechanism was discovered in $a-SiO_2$ [28]. Here, an electron located in the conduction band of $a-SiO_2$ spontaneously localizes at a site with a strained O-Si-O angle. This localization of charge is associated with an energy gain of 0.7-1.7eV (depending on the environment in the amorphous host) and is hence reasonably stable at room temperature. The excess charge induces a polarization field in its vicinity causing a distortion of the host material, the charge is hence self-trapped similar to small polarons known in crystalline materials.

While in a-SiO₂ self-trapped holes are only weakly bound and unstable above 180K [29], we find that in a-Si₃N₄ both electrons and holes can self-trap with significant binding energies. As shown in Fig. 13, the bandgap of the structure is initially free of any electronic states, however, after injecting a charge, it self-traps and forms a localized state in the bandgap. While we observe that the excess charges can localize at various different sites like Si atoms or elongated Si-N bonds, further investigations are necessary to understand the exact mechanisms causing the spontaneous charge trapping. However, our findings suggest that intrinsic charge trapping plays a major role for the reliability of Si₃N₄ films.

4 Defects in Si_xGe_{1-x}O₂

Silicon-germanium alloys are widely used in nanoelectronics, e.g. to increase the mobility of silicon by strain-engineering. However, compared to Si, the native oxide of Si_xGe_{1-x} is less stable than a-SiO₂ and exhibits larger defect concentrations. This poses a reliability challenge for SiGe devices. Here, based on our previous work on a-SiO₂, we present a first-principles study on oxygen vacancies in amorphous Si_xGe_{1-x}O₂ for various germanium concentrations.

4.1 Structure Creation and Verification

Similar to Si_3N_4 we could not find a suitable classical forcefield for a melt-quench MD to create amorphous oxide samples. Given the chemical similarities between Si and Ge, we started from an already prepared a-SiO₂ sample with 216 atoms and randomly replaced Si with Ge for



Figure 14: (left) Total neutron structure factors of a-SiO₂ and a-GeO₂ compared to experiment [30]. The black, solid lines are the results from the calculated models while the red markers with dashed lines are data points from experiment. (right) The simulated structure factors for all concentrations of Si_xGe_{1-x}O₂ considered in this paper which show a smooth transition from the structure factor of a-GeO₂ to a-SiO₂.

Concentration	Ge–O	σ (Ge–O)	Si–O	$\sigma(\text{Si-O})$	ρ	E_{g}
0%	1.744	0.010	N/A	N/A	3.37	5.50
25%	1.742	0.011	1.615	0.0099	3.08	5.79
50%	1.741	0.013	1.615	0.010	2.83	6.17
75%	1.736	0.014	1.614	0.012	2.52	6.64
100%	N/A	N/A	1.613	0.013	2.20	8.22

Table 1: Structural and electronic properties of the simulated Si_xGe_{1-x}O₂ cells. The concentration indicates the number percentage of Si atoms. Ge–O and Si–O indicate the respective bond lengths with their standard deviations, σ , both of which are measured in Å. ρ is the cell density measured in g/cm³ and E_g indicates the band gap which was measured in eV.

different Si concentrations (x=0%, 25%, 50%, 75%, 100%). Subsequently, the $Si_xGe_{1-x}O_2$ structures were fully relaxed within DFT, meaning that both the geometry and the cell vectors were optimized to remove residual forces and strain. As shown in Fig. 14, this approach is justified and gives good agreement with experimental data [30]. Table 1 shows the calculated properties for Si_xGe_{1-x}O₂ in various concentrations. The calculated band gaps, taken as the difference between the energies of the highest occupied and lowest unoccupied Kohn-Sham levels, for a-SiO₂ and a-GeO₂ are slightly underestimated compared to experimental values in the literature. There is a notable large drop in band gap from 100% to 75% Si that has previously been reported in the literature [31]. Since a-SiO₂ has a larger band gap than a-GeO₂ and that the addition of Ge atoms contribute to the bottom of the conduction band, adding a Ge atom to a-SiO₂ introduces atomic orbitals that sit below the a-SiO₂ conduction band. These states would be localized on the Ge atom and could be considered as a substitutional impurity defect at very low concentrations. A band begins to form that widens with the number of added Ge atoms as the concentration of Ge atoms increases. Therefore, the initial introduction of Ge appears as a large drop in the band gap due to the lower Ge antibonding states, followed by a widening of the band. This also explains why the band gap changes less drastically between 75% to 0% Si atoms.

4.2 Oxygen Vacancies in Si_xGe_{1-x}O₂

To model oxygen vacancies in $Si_xGe_{1-x}O_2$, one oxygen atom was removed from the defect free systems described above followed by a minimization of the system's total energy with respect to its atomic coordinates. For each $Si_xGe_{1-x}O_2$ concentration, the oxygen vacancy was introduced at all 144 possible sites. As each vacancy can trap either one hole or electron, it was modeled in its neutral, positive, and negative charge states.

4.2.1 Neutral Charge state

An oxygen atom was removed from all possible sites between Si and Ge atoms in the aforementioned concentrations of $Si_xGe_{1-x}O_2$ and the structures were subsequently optimized. The resulting atomistic structures were qualitatively similar across all concentrations. An example of the atomic structure and the highest occupied molecular orbital (HOMO) is shown in Fig. 15. As is the case for the vacancy in pure $a-SiO_2$ and $a-GeO_2$, the HOMO is mostly localized in a bonding orbital between the two atoms at the vacancy; however, some of the HOMO is delocalized in the p orbitals of nearby O atoms.

It was found that the quantitative behavior of the defect was defined not by the various concentrations of $Si_xGe_{1-x}O_2$ determined by x, rather by the atoms composing the vacancy. We, therefore, describe the structural features by the atoms surrounding the defect. The bond length for a vacancy surrounded by Ge–Ge, Si–Si, and Si–Ge was found to be 2.51 Å, 2.41 Å, and 2.45 Å on average. The vacancy bond length was found to be extremely stable and predictable, with a standard deviation of below 0.1 Å for all vacancy types. The bond lengths here are similar to those recently reported in the literature [32]; however, older papers report that the Ge–Ge dimer tends to be shorter than Si–Si [33]. The neutral vacancy was found to introduce a state just above the top of the valence band, an example of which is shown in Fig. 15. The one-electron Kohn-Sham (KS) level was found to sit 0.53 eV, 0.76 eV, and 0.61 eV on average above the valence band for the Ge–Ge, Si–Si, and Si–Ge dimers, and they had a standard deviation no higher than 0.2 eV. The relationship between the dimer length and the formation energy is shown in the left panel of Fig. 16. It is clear that the formation energy is strongly correlated with the dimer's length for the three different vacancy configurations.



Figure 15: Atomistic structure and orbitals of the vacancy's various charge states in $Si_xGe_{1-x}O_2$. The Si, Ge and O atoms are represented by pink, yellow and red spheres, respectively. The top left is the highest occupied orbital of the neutral vacancy. The top right is the negatively charged vacancy's spin density. The bottom left and right show the spin density of the positively charged vacancy in the dimer and puckered configurations, respectively.



Figure 16: Scatter plot of the oxygen vacancy's formation energy in $Si_xGe_{1-x}O_2$ against the distance of the atoms surrounding the vacancy. The left, middle, and right panels show results for the neutral, negative, and positive charge states. Green, yellow, and blue circles are vacancies composed of Ge–Ge, Si–Si, and Si–Ge dimers, respectively.

4.2.2 Negative Charge State

Using the neutral configurations above, an electron was added to each configuration and their geometries were optimized. The majority resulted in the electron localizing on the dimer as depicted in Fig. 15. Qualitatively, the structure of the negatively charged vacancies was the same, regardless of the $Si_xGe_{1-x}O_2$ concentration or the atoms surrounding the vacancy, as was the case for its neutral analog. The additional electron was localized between the two atoms surrounding the vacancy as shown in Fig. 15. The distances between the vacancy's atoms were 2.84 Å, 2.57 Å, and 3.12 Å for the Ge–Ge, Si–Si, and Si–Ge dimers. The bond length of the Si–Si dimer compares very well with a literature value of 2.60 Å in pure a-SiO₂, showing that the bond length does not vary much in the hybrid $Si_xGe_{1-x}O_2$ systems.

The one-electron KS levels of the additional electron measured from the top of the relevant $Si_xGe_{1-x}O_2$ valence bands were 3.81 eV, 5.7 eV, and 3.82 eV for the Ge–Ge, Si–Si, and Si–Ge dimers. The negative Ge–Ge configuration was far more stable than its Si counterpart whose KS level is rather high. Trapping an electron at the Si–Si vacancy compared to the other dimers was more unlikely to happen as the Ge content increased due to the KS level being closer to the bottom of the conduction band. In those cases, the electron preferentially delocalizes into a band state. The negative vacancy's formation energies are shown in the middle panel of Fig. 16 with respect to the dimer length. The formation energy is calculated with respect to an electron reservoir at the top of the $Si_xGe_{1-x}O_2$ valence band, hence the higher values. Similar to the neutral vacancy, its negative counterpart shows a dependence of its formation energy on the dimer distance, regardless of the atoms involved. The $Si_xGe_{1-x}O_2$ concentration also had no discernible effect on the calculated formation energies.

4.2.3 **Positive Charge States**

A hole was added to the neutral configurations followed by an optimization to calculate the positively charged vacancies. Regardless of the Si concentration, the positively charged systems remained qualitatively similar. This was similar to the neutral and negative vacancies. However, unlike the other charge states, the positive vacancies showed two discernible structures. An example of each is shown in Fig. 15. We refer to these two configurations as the dimer (bottom-left panel of Fig. 15) and the puckered (bottom-right panel of Fig. 15) configurations, similar to their analogs in pure $a-SiO_2$. The dimer configuration shows shorter

distances between the surrounding atoms, with the Ge–Ge, Si–Si, and Si–Ge dimers showing 2.92 Å, 2.88 Å, and 2.79 Å, respectively. Their puckered counterparts have distances of 4.11 Å, 3.91 Å, and 4.12 Å, respectively. The Si–Si dimer length is close to the corresponding value of 2.9 Å for vacancies in a-SiO₂ previously reported in literature [34].

For the dimer configuration, the distance increases compared to the neutral state as there is now one fewer electron in its bonding orbital resulting in a weaker bond. The dimer introduces a singly occupied KS orbital in the bandgap, which sits 0.65 eV, 0.71 eV, and 0.47 eV above the corresponding valence band for the Ge–Ge, Si–Si, and Si–Ge dimers, respectively. The puckered configuration's electronic structure is qualitatively different. Instead of an electron being shared with the atoms surrounding the vacancy, a single atom has a dangling bond. It can be easily identified as it is more positively charged than the other equivalent atoms in the system. The bottom panel of Fig. 15 shows an example of the puckered structure, where the electron is in a dangling bond on the Ge atom on the left side. It was found that the positively charged Si ion could form a weak interaction with an oxygen due to this relaxation. This electrostatic interaction between the positively and negatively charged Si and O ions is favorable and reduces the energy of the system. However, an O ion is not always present behind the Si ion, in which case this interaction does not occur and the Si or Ge ion is bonded to its three neighbors in a planar configuration. We note that when the atoms surrounding the vacancy are Si-Ge and the system is in the puckered configuration, the dangling bond was always localized on the Ge ion while the hole is on the Si ion, similar to the structure shown in the bottom panel of Fig. 15.

The formation energies of the positively charged vacancies are rather varied, reflecting the two possible configurations. The right panel of Fig. 16 shows how the formation energy varies with the distance between the two ions surrounding the vacancy and distinguishes between the two configurations, dimer and puckered. The charge reservoir is set to the top of the valence band of the relevant Si_xGe_{1-x}O₂ system. One immediately sees that relative to the neutral and negative charge states, the positive states are spread out over a much larger range of interatomic distances, due to their two possible configurations. The dimer configurations can easily be identified as they form clusters at lower distances. The dimer configurations also show a positive correlation with distance, with the formation energy increasing rapidly as the interatomic distance increases, since the binding energy provided by the Si-Si bond reduces substantially with distance. The much larger distances typically correspond to the puckered configurations which show a weak inverse correlation. The existence of these stabilizing O atoms allows for such an increased distance between the two ions. This extra stability means that the puckered configurations can be lower in energy than the dimer. Curiously, the atoms surrounding the vacancy showed a difference in the proportion of the dimer to puckered configurations. For Si-Si atoms, 71% were dimers and 29% were puckered. The Ge-Ge dimers had a rather different proportion, with 35% preferring to be in the dimer configuration and 65% in the puckered. The Si–Ge configurations sat very much in the middle of these two, with 57% dimer configurations and 43% puckered.

Conclusions

In this deliverable we employ density functional theory (DFT) to get insights into the atomistic mechanisms of silicon oxidation and the formation of defects in important materials for nanoelectronic devices like amorphous SiO_2 , Si_3N_4 and $Si_xGe_{1-x}O_2$.

We analyzed the various steps of thermal oxidation of an Si(100) surface using a combination of DFT and density functional based tight-binding (DFTB) in order to cover several timescale. We showed that the initial oxidation process happens spontaneously and is associated with a charge transfer to the approaching O₂ molecule. After the surface is sufficiently covered with O, the reaction slows down and proceeds via so-called molecular precursor states. After the surface and formed oxide become chemically inert, the oxidation enters the well-known Deal-Grove regime, in which O₂ diffuses through the a-SiO₂ network and only reacts at the Si/SiO₂ interface with a charge transfer similar to the initial oxidation at the clean surface. These insights are important for the kinetic Monte-Carlo simulations conducted in D5.6 and the demonstrator in WP6.

We further investigated common defects in $a-SiO_2$ like the oxygen vacancy, the hydrogen bridge and the hydroxyl-E' center. We demonstrated that these defects are in general amphoteric, meaning they can act as hole and electron traps simultaneously. We showed that these defects can be described within a 7-state Markov model and provided a detailed analysis of the reactions between the different states. These findings will be integrated into the TCAD models within WP6 to improve the description of oxide reliability beyond the current state of the art.

In less structured materials like Si_3N_4 we find a tendency of injected charges to spontaneously localize and form both electron and hole polarons. Electrically, these self-trapped charges can behave similarly to ordinary charged defects and are thus highly relevant for the reliability in these materials.

Since SiGe is a promising material in nanoelectronics and is also studied within the scope of WP2 and WP3, we also provide a study on oxygen vacancies in the native oxide $Si_xGe_{1-x}O_2$. We studied these defects for various Si concentrations and found that their behavior is mostly determined by the Si and Ge atoms in the vicinity of the defects instead of the overall concentration of Si or Ge.

References

- L. Cvitkovich, D. Waldhoer, A.-M. El-Sayed, M. Jech, C. Wilhelmer and T. Grasser, "Dynamic modeling of Si (100) thermal oxidation: Oxidation mechanisms and realistic amorphous interface generation," *Applied Surface Science*, vol. 610, p. 155378, 2023.
- [2] Y. J. Lee, S. Kim, C.-S. Hwang, C. Lee and C. Hwang, "Reconstruction on Si(100) surfaces," *Physical Review B*, vol. 50, no. 15, p. 11204, 1994.
- [3] R. S. Mulliken, "Electronic Population Analysis on LCAO–MO Molecular Wave Functions.
 II. Overlap Populations, Bond Orders, and Covalent Bond Energies," *The Journal of Chemical Physics*, vol. 23, p. 1841, 1955.
- [4] K. Kato and T. Uda, "Chemisorption of a single oxygen molecule on the Si(100) surface: Initial oxidation mechanisms," *Physical Review B*, vol. 62, p. 15978, 2000.
- [5] D. Kaya, R. J. Cobley and R. E. Palmer, "Combining scanning tunneling microscope (STM) imaging and local manipulation to probe the high dose oxidation structure of the Si(111)-7×7 surface," *Nano Research*, vol. 13, pp. 145-150, 2020.

- [6] N. Salles, N. Richard, N. Mousseau and A. Hemeryck, "Strain-driven diffusion process during silicon oxidation investigated by coupling density functional theory and activation relaxation technique," *Journal of Chemical Physics,* vol. 147, p. 054701, 2017.
- [7] Y.-C. Liao, A. M. Nienow and J. T. Roberts, "Surface Chemistry of Aerosolized Nanoparticles:Thermal Oxidation of Silicon," *The Journal of Physical Chemistry B*, vol. 110, p. 6190–6197, 2006.
- [8] B. Hourahine, "DFTB+, a software package for efficient approximate density functional theory based atomistic simulations," *The Journal of Chemical Physics,* vol. 152, p. 124101, 2020.
- [9] C. Koehler, Z. Hajnal, P. Deak, T. Frauenheim and S. Suhai, "Theoretical investigation of carbon defects and diffusion in α-quartz," *Physical Review B*, vol. 64, p. 085333, 2001.
- [10] R. L. Mozzi and B. E. Warren, "The structure of vitreous silica," *Journal of applied crystallography*, vol. 2, no. 4, pp. 164-172, 1969.
- [11] 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," *Physical Review B*, vol. 100, p. 195302, 2019.
- [12] E. Kobeda and E. A. Irene, "Intrinsic SiO2 film stress measurements on thermally oxidized Si," *Journal of Vacuum Science & Technology B,* vol. 5, p. 15, 1987.
- [13] B. E. Grove and A. S. Deal, "General Relationship for the Thermal Oxidation of Silicon," *Journal of Applied Physics,* vol. 36, p. 3770, 1965.
- [14] A. Bongiorno and A. Pasquarello, "Multiscale modeling of oxygen diffusion through the oxide during silicon oxidation," *Physical Review B*, vol. 70, p. 195312, 2004.
- [15] H. Jonsson, G. Mills and K. Jacobsen, "Nudged elastic band method for finding minimum energy paths of transitions," *Classical and Quantum Dynamics in Condensed Phase Simulations*, pp. 385-404, 1998.
- [16] A. P. Thompson, "LAMMPS a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales," *Computational Physics Communications,* vol. 271, p. 10817, 2022.
- [17] A. C. T. v. Duin, A. Strachan, S. Stewman, Q. Zhang, X. Xu and W. A. Goddard, "ReaxFFSiO Reactive Force Field for Silicon and Silicon Oxide Systems," *Journal of Physical Chemistry A*, vol. 107, no. 19, p. 3803–3811, 2003.
- [18] R. A. B. Devine and J. Arndt, "Si—O bond-length modification in pressure-densified amorphous SiO2," *Physical Review B*, vol. 35, p. 9376(R), 1987.
- [19] D. Price and J. Carpenter, "Scattering function of vitreous silica," *Journal of Non-Crystalline Solids*, vol. 92, pp. 153-174, 1987.
- [20] S. Dannefaer, T. Bretagnon and D. Kerr, "Vacancy-type defects in crystalline and amorphous SiO2," *Journal of Applied Physics*, vol. 74, p. 884, 1993.

- [21] C. Wilhelmer, D. Waldhoer, M. Jech, A.-M. B. El-Sayed, L. Cvitkovich, M. Waltl and T. Grasser, "Ab initio investigations in amorphous silicon dioxide: Proposing a multi-state," *Microelectronics Reliability*, vol. 139, p. 114801, 2022.
- [22] 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," *Physical Review Letters*, vol. 114, p. 115503, 2015.
- [23] 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," *Physical Review B*, vol. 92, p. 014107, 2015.
- [24] W. Goes, Y. Wimmer, A.-M. El-Sayed, G. Rzepa, M. Jech, A. Shluger and T. Grasser, "Identification of oxide defects in semiconductor devices: A systematic approach linking DFT to rate equations and experimental evidence," *Microelectronics Reliability*, vol. 87, pp. 286-320, 2018.
- [25] D. Waldhoer, C. Schleich, J. Michl, B. Stampfer, K. Tselios, E. G. Ioannidis, H. Enichlmair, M. Waltl and T. Grasser, "Toward Automated Defect Extraction From Bias Temperature Instability Measurements," *IEEE Transactions on Electron Devices*, vol. 68, pp. 4057-4063, 2021.
- [26] S. R. Billeter, A. Curioni, D. Fischer and W. Andreoni, "Ab initio derived augmented Tersoff potential for silicon oxynitride compounds and their interfaces with silicon," *Physical Review B 73,* vol. 73, p. 155329, 2006.
- [27] J. Bauer, "Optical properties, band gap, and surface roughness of Si3N4," *physica status solidi (a),* vol. 39, pp. 411-418, 1977.
- [28] A.-M. El-Sayed, M. B. Watkins, V. V. Afanas'ev and A. L. Shluger, "Nature of intrinsic and extrinsic electron trapping in SiO2," *Physical Review B*, vol. 89, p. 125201, 2014.
- [29] D. L. Griscom, "Self-trapped holes in amorphous silicon dioxide," *Physical Review B*, vol. 40, p. 4224(R), 1989.
- [30] M. Micoulaut, L. Cormier and G. S. Henderson, "The structure of amorphous, crystalline and liquid GeO2," *Journal of Physics: Condensed Matter,* vol. 18, p. R753, 2006.
- [31] K. Baral, P. Adhikari and W.-Y. Ching, "Ab initio Modeling of the Electronic Structures and Physical Properties of a-Si1-xGexO2 Glass (x = 0 to 1)," *Journal of the American Ceramic Society*, vol. 99, pp. 3677-3684, 2016.
- [32] N. Richard, S. Girard, L. Martin-Samos, V. Cuny, A. Boukenter, Y. Ouerdane and J.-P. Meunier, "First principles study of oxygen-deficient centers in pure and Ge-doped silica," *Journal of Non-Crystalline Solids*, vol. 357, pp. 1994-1999, 2011.
- [33] T. Tamura, G.-H. Lu, R. Yamamoto and M. Kohyama, "First-principles study of neutral oxygen vacancies in amorphous silica and germania," *Physical Review B*, vol. 69, p. 195204, 2004.
- [34] S. Mukhopadhyay, P. V. Sushko, A. M. Stoneham and A. L. Shluger, "Modeling of the structure and properties of oxygen vacancies in amorphous silica," *Physical Review B*, vol. 70, p. 195203, 2004.

[35] T. Aiyama, T. Fukunaga, K. Niihara, T. Hirai and K. Suzuki, "An X-ray diffraction study of the amorphous structure of chemically vapor-deposited silicon nitride," *Journal of Non-Crystalline Solids*, vol. 33, no. 2, pp. 131-139, 1979.