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ICT Project No 871813 **MUNDFAB** Modeling Unconventional Nanoscaled Device FABrication

D5.2: Provisional Atomistic Catalogue of Chemical Reactions Relevant for Defect Formation

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Abstract

The main task of WP5 is the identification and description of the fundamental reactions of defect formation within the various processing steps involved in the manufacturing of modern nano-electronic devices. Within the first months of the reporting period, the activities have been coordinated between the different workpackage tasks. Due to the extensive experience and knowledge of the involved partners new simulation approaches have been quickly developed and employed. The main focus on this first period has been on the complex and various mechanisms involved in thermal oxidation as well as on the statistical investigation of the intrinsic and hydrogen related defects in the amorphous SiO₂ network. Furthermore, substantial efforts have been made to establish a machine learning based framework, capable of predicting important defect characteristics with reasonable accuracy in an efficient way. These results are of utmost importance for the kinetic Monte Carlo tool developed in Task 5.1 which ultimately provides the benchmark models for the amorphous SiO₂ and the Si/SiO₂ interface structures and also the TCAD framework of WP6 to accurately include the effects and implications of defects in the oxide layers.

1 Oxidation

The thermally grown Si/SiO₂ system is one of the most studied interface systems, theoretically and experimentally. Nevertheless, the full picture of oxidation is a rather complex phenomenon ranging over a broad timescale and exhibits various mechanisms such as charge transfer reactions. Hence, it was necessary to develop a multiscale simulation approach to fully capture the peculiarities of each individual step. The complete oxidation process can be divided into three phases: First, the initial dissociation of the O₂ molecule and the subsequent adsorption of the oxygen molecules on the reconstructed Si(100) surface. The partial to full coverage of the crystalline silicon surface. Third, the amorphization process which proceeds layer-by-layer due to the supply of oxygen molecules and atoms. For each mechanism a different hierarchical method, ranging from ab initio density functional theory to tight binding and up to classical force fields, is employed due to the different timescales available and the involved number of atoms.

1.1 O₂ dissociation and adsorption

The purpose of these simulations is to identify the initial oxidation reaction on a (2x1) reconstructed Si(100) surface [1]. The starting point is an O₂ molecule above the reconstructed surface, for which the undercoordinated Si atoms formed rows of alternating up- and down-dimers to compensate for the unpaired electrons (one electron is transferred from the bottom to the top atom resulting in an approximate ionic character of the Si-Si bond). Subsequently, ab initio molecular dynamics simulations (AIMD) were conducted within the CP2k package [2], employing a DVZP basis set, at a temperature of 300K within a microcanonical ensemble. The total simulation time has been set to 1.5ps with a step size of 0.5fs. The results for this simulation can be seen in Fig. 1.

In an initial step the O_2 molecule travels towards a valley between two dimer rows and attaches to one of the two topmost Si atoms. This leads to a hybridization of the $O_2 \pi^*$ orbitals (the O_2 in its ground state is a triplet configuration where both π^* orbitals are occupied by single, unpaired electrons) with the surface states of the Si slab. After about 100-200fs one of the two Si atoms, where the O_2 molecule initially adsorbed, donates one electron to the π^* orbitals of



Figure 1: The results of the AIMD simulation. The oxygen molecule approaches the reconstructed Si surface and captures an electron from the topmost silicon atom of the dimer configuration. Subsequently the O_2 molecule dissociates and the resulting oxygen atoms desorb on the Si surface in either a dimer or a backbone site.

the oxygen molecule. This can be seen in Fig .1 as the rapid change of charge state of the two oxygen atoms, becoming negatively charged, and the surrounding Si atoms donating in total one electron. Subsequently, the oxygen molecule is left in an excited state spontaneously dissociates without a notable barrier. Finally, the two O atoms remain at the dimer or backbone site of the silicon atom.

1.2 Oxygen coverage of the Si surface

With the introduction of oxygen on the surface, the (mainly surrounding) silicon atoms experience an additional strain which leads to an electronic reconfiguration and slightly undercoordinated and electrophilic sites. Hence, a broader spectrum of barrierless chemisorption sites available for subsequent O₂ molecules. In order to simulate larger structures and longer timescales, we employed a density functional based tight binding approach (DFTB) implemented in the DFTB+ package [3]. Molecular dynamics simulations with the intention of full surface coverage (i.e. a fully passivated surface) were run and yield, after a geometry optimization, two distinct configurations, see Fig. 2a and 2b. The two configurations can be identified as the zig-zag (Fig. 2a) and the ring (Fig. 2b) configuration. The ring structure is the energetically most stable one with the lowest energy, however, the zig-zag configuration is only about 0.35eV/dimer higher in energy, rendering it another metastable configuration at elevated temperatures. Furthermore, we found some additional slightly disordered configurations, see for example Fig. 2c, where individual oxygen atoms actually moved within a back-bonded configuration. Interestingly this configuration is around 0.2eV lower in energy than the zig-zag configuration, however still around 0.15eV higher than the ring structure. Hence, at elevated temperatures such configurations can be considered as additional metastable surface coverages. Nevertheless, all resulting configurations clearly show that the oxygen atoms remain within Si-Si bonds at the surface and do not spontaneously diffuse within the Si network. This indicates that the process of oxidation is indeed a layer-bylayer mechanism, in which subsequent silicon layers are only oxidized upon further supply of



Figure 2: Three distinct configurations for a full oxygen coverage of the Si(100) surface. From left to right : (a) The zig-zag structure, (b) the ring configuration, (c) a slightly disordered (metastable) variant of the zig-zag configuration where individual O atoms moved within the back-bonded Si-Si bonds.

 O_2 molecule on the surface which causes the already existing oxygen atoms to penetrate further into the crystalline silicon.

1.3 Amorphization

In order to provide a full picture of the oxidation and amorphization of thin film SiO_2 layers, including the Si/SiO_2 interface region, the aforementioned simulation approaches are not applicable due to the extensive timescales required for such calculations. Hence, we used a previously parameterized extended Stillinger-Weber potential [4], particularly parametrized to mimic the oxidation mechanism including a penalty parameter for the different oxidation states, within the molecular dynamics engine LAMMPS [5]. The procedure is as follows: First, a Si(100) slab with a total height of 40nm and 1792 atoms, with the last layer being fixed, has been equilibrated at a temperature of T=500K. Subsequently, 10 oxygen atoms are inserted



Figure 3: Snapshots of the oxidation simulations where around half of the available Si atoms have been oxidized (left), and almost the entire slab is consumed by SiO_2 (middle). A close-up of the direct interface region between crystalline Si and amorphous SiO_2 .

between Si-Si bonds directly at the surface, where after each insertion the geometry gets optimized to avoid any artificial strain. After 10 atoms have been inserted, a MD run is conducted with 100000 steps at the given temperature to facilitate bond breaking and reconfiguration which leads to the amorphization of the structure. Hence, oxidizing the silicon slab happens in portions of 10 O atoms with intermediate MD runs. Only if the silicon layer has been fully oxidized, i.e. SiO_4 tetrahedrons have been formed, the next layer will be filled with oxygen atoms. Fig. 3 shows the images of a Si/SiO_2 interface system where half of the slab (a) has been oxidized, and almost the full silicon structure transformed into SiO_2 (b), respectively.

One can see that the interface between Si and SiO_2 is not fully abrupt and that the Si positions around two layers away from the interface still deviate from their original position within the crystalline lattice. However, this was confirmed by previous experimental studies using ion backscattering measurements as well as optical spectroscopy. Furthermore, this methodology results in a non-stochiometric SiO2 structure and will be used to extract the intrinsic defect concentration. The necessity of larger structures including well beyond 10000 atoms, will be evaluated for this purpose. One can conclude that the utilized approach agrees well with the experimental perceptions and the resulting models and insights can be used to improve the developed kinetic Monte Carlo (kMC) code of WP5.1 and furthermore act as an additional benchmark of the structures used in WP5.2.

2 Defects in SiO₂

Intrinsic point defects, such as the oxygen vacancy (OV) are unavoidable in the amorphous SiO₂ network. Additionally, hydrogen related oxide defects have gained lots of interest in the recent past and are believed to be responsible for device degradation issues such as the bias temperature instability (BTI).

Once hydrogen is introduced into the system, i.e. during a forming gas anneal, it can diffuse through the oxide and trigger additional reactions and create point defects such as the hydrogen bridge (HB) and the hydroxyl E' (HE') center. The HB is a transformed OV where the H atom attaches to one of the Si atoms, whereas for the HE' center the hydrogen breaks a preexisting Si-O bond and forms a hydroxyl group together with one undercoordinated Si atom.

All three defect configurations have active defect levels inside the SiO_2 band gap, i.e. their charge transition levels -/0 and 0/+ are within the band gap of the oxide, and hence can interact with charge carriers in the channel of a MOSFET. Upon charge capture and emission, which is properly described using non-radiative multiphonon theory, defects undergo structural relaxations which is an important measure and characteristics in the modeling framework. Thus, the initial modeling efforts have been made to identify and characterize a larger number of defect configurations for the OV, the HB, and the HE' within amorphous bulk SiO₂. These are crucial information used in WP6 and the corresponding TCAD framework.

2.1 Methodology

The SiO_2 models including the defect configurations have been calculated using density functional theory (DFT) using the Gaussian plane wave code CP2k [2]. GTH pseudopotentials

in conjunction with a double-zeta basis set and an energy cutoff of 800Ry have been employed to ensure well converged results. The nonlocal hybrid functional PBE0 in combination with an auxiliary basis set has been used to maintain a high level of accuracy and reasonable computational efforts. All geometry optimizations have been performed using the BFGS algorithm where forces on the individual atoms have been reduced down to 0.025eV/A.

The initial host material, i.e. the defect free SiO2 model, contains 216 atoms, see Fig. 4, and has been created using molecular dynamics and the well-known melt and quench technique in conjunction with the classical force field ReaxFF [6]. The resulting structures have been subsequently optimized to ensure a strain free bulk SiO₂ model.



Figure 4: Well optimized and defect free bulk SiO2 model with periodic boundary conditions.

2.2 Results

In the following, the three discussed defect types, the OV, HB and H*E*', see Fig. 4, are analyzed for three different charge states, Q=0/-1/+1. The initial defects have been created in the following way: For the OV, one single oxygen atom has been removed, for the HB the oxygen atom was replaced by a hydrogen atom, while for the H*E*' center a hydrogen atom was placed in the direct vicinity of a bridging O atom. This procedure was repeated for each of the 144 oxygen atoms in the SiO₂ structure and subsequently relaxed in the different charge states.

First, the formation energy E^{form} of a defect has been calculated, which is given by

$$E^{form} = E_Q^{tot} - E_{bulk}^{tot} - \sum_i \mu_i n_i + qE_F + E^{cor}$$
(1)

where E_Q^{tot} is the total energy of the system with the defect in charge state Q, E_{bulk}^{tot} is the total energy of the defect free neutral bulk model, $\mu_i n_i$ is the chemical energy needed to add or remove atoms of kind *i* to the bulk in order to create a defect, qE_F is the elementary charge times the Fermi level, and E^{cor} is a correction term due to the periodic boundary conditions and in combination with a charged system.

The formation energies of the neutral defect configurations are calculated with respect to the pristine bulk system. However, this might overestimate their values, since they are typically naturally formed during the oxidation process, which cannot be included here. For the HB and the HE' center the precursor configurations are an oxygen vacancy and a bridging oxygen atom, respectively. The OV and the HE' center formation energies can be properly described

by a normal distribution, while for the HE' center on the other hand, the distribution of formation energies is highly asymmetric, and hence was fitted with a Weibull distribution.

For all defect configurations we distinguish between normal and puckered, or back-bonded, configurations. For such a puckered configuration the oxygen atom moves through the plane of the adjacent silicon atoms and back-bonds to another silicon atom. Our findings show that the puckered OV configuration has substantially higher formation energy and it is thus unlikely to form within our calculations.

The charge transition level (CTL) for the different defect configurations can be calculated by comparing the formation energies (1) of different charge states. The Fermi level is with respect to the valence band maximum which is assumed to be the highest occupied Kohn-Sham orbital of the bulk system. The correction term E^{cor} was approximated to be 0.35eV according to the scheme of Makov and Payne [7]. The CTL corresponds to the Fermi level where the charged and neutral formation energy possesses the same value, and hence are equally likely. It is one of the fundamental characteristics of a defect as it can be detected by electrical measurements and its alignment with the carrier reservoir, i.e. the channel of the device, substantially affects the reliability behavior of the technology. The CTLs for the three different defect configurations and the transitions +/0 and 0/- have been caclulated. The band gap of the silicon bulk is around 1.2eV according to our DFT calculations. The calculated values nicely match with the wellknown values for the band alignment between Si and SiO2. Furthermore, only defects are considered for the CTL calculations where the additional charge could be properly localized at the defect site for both charge states. The accumulated CTL for the HB and the HE' center resemble a normal distribution, while the CTL of the unpuckered OV were again fitted with a Weibull distribution for both charge transitions. For the OV defects, the majority of CTLs for both charge transitions are far below the valence band (+/0) or far above the conduction band (-/0) of the silicon bulk. Hence, it is very unlikely for them to interact with the carrier reservoir. The only exception are OV defects in the puckered configuration, with their CTLs being inside the band gap of silicon. This result confirms the assumption that the OV is not responsible for charge trapping processes during operation in MOSFET devices. The other two defect candidates however possess reasonable defect levels close to the silicon valence or conduction band edge. The peaks of the HB distributions are both close to the band edges of the substrate, similarly to the electron traps of the HE' center, while the hole traps of HE' center are distributed largely across the silicon band gap.

Hence, it is assumed that the HB in combination with the HE' center are mainly responsible for charge trapping effects such as bias temperature instability in silicon based MOSFET devices. These results will aid the TCAD description in WP6.

Additionally, we have analyzed the correlation of the CTLs or formation energy and geometrical properties of the defects. This information reflects the likelihood of a certain CTL and links it to structural characteristics which can be beneficial for the kMC description in WP5.1. Hence, we have analyzed the correlation of the formation energies and the calculated CTLs. For the OV a meaningful measure is the distance between the two silicon atoms before the oxygen atom has been was removed, for the HB a correlation between two silicon atoms of an OV before the hydrogen was attached and the CTL/ E^{form} was found, while the HE' center it shows a strong dependence on the distance between a silicon and oxygen atom before the hydrogen was bonded to the oxygen atom and formed a hydroxyl group.

Unpuckered oxygen vacancies with CTLs closer to the band edges of the silicon substrate are less likely to form and thus OVs tend to play an even smaller role in reliability issues. Hydrogen bridges are preferably forming at prolonged Si-Si distances of an OV. The CTLs for the HB hole traps with the lowest formation energies are below the valance band maximum of silicon while the CTLs in the middle of the band gap are less likely to form. This is similar for HB electron traps, where the defects with the lowest E^{form} have CTLs close to the conduction band edge of the substrate while for higher formation energies the CTLs tend to be located in the band gap. For the HE center defects, the hole trapping defects that are most likely to form are also the defects which are most likely to capture a hole from the substrate. The CTLs of the electron traps are distributed close to the conduction band edge for the entire E^{form} range.

3 Application of Machine Learning

The above defect studies require extensive computational efforts due to the use of DFT. Hence, the main disadvantage is that such studies are limited to small systems on the order of a few hundred atoms, or smaller statistics. In this context, machine learning (ML) offers very promising solutions to perform the required calculations, by achieving results with an accuracy comparable to DFT, while requiring only a small fraction of its computational cost.



Figure 5: Left: Distribution of the formation energies, together with its mean and the standard deviation. Right: Correlation between the formation energy and the characteristic length of the initial Si-O bond which is broken due to the attachment of a hydrogen atom.

Hence, two approaches have been developed to aid the study of modern devices reliability: (1) a ML solution to predict the formation energy of defects and (2) a ML solution to predict the structure of these defects. In both cases, the material under consideration was amorphous SiO_2 and the defects under consideration were hydroxyl *E*' center configurations. Studying these defects, especially their formation during device processing, is of great importance, particularly with respect to WP5.1. In order to build a reliable ML model to predict electronic properties, it is first necessary to adequately train the framework. Hence, in total 16 SiO_2 models have been used from the above defect study and overall 1271 hydroxyl *E*' center defects have been calculated within DFT and the GGA approximation. Within Fig. 5 one can see the distribution of formation energies and their correlation to the most important structural measure, the initial Si-O bond length of the pristine SiO_2 bulk system.

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3.1 Prediction of Formation Energies

As previously mentioned, we first developed a ML based solution to predict the formation energies of defects. The goal was to achieve predictions as accurate as possible, while drastically reducing the computational costs.

Our proposed presented in applied to formation hydroxyl E in a-SiO₂. The produce ML property from atomistic represent the testing way which is



Figure 6: Proposed workflow to predict a characteristic feature of the defect of interest. The environment around the defect is represented by a descriptor and subsequently used within the ML model to predict the formation energy of the defective site.



Figure 7: Error distribution and mean absolute error of the predictions of formation energies using 9 combinations of models and descriptors.

with the selected ML model. This representation is done with a descriptor. In this work, the descriptors which were considered are atom-centered symmetry functions (ACSF) and smooth overlap of atomic positions (SOAP), as implemented in the python package DScribe [8]. We also considered our own descriptor which is purely based on geometrical measures, namely bond-lengths and bond-angles (BLBA) - developed for this purpose by our research team, see [9].

Once the structures in the training and testing datasets are properly represented, the next step is to train the ML model. The ML models selected for this application were neural network (NN), kernel ridge regression (KRR) and decision tree (DT), as implemented in the scikit-learn software package [10]. These models were selected based on their versatility and their common use in the relevant literature. In total, 9 different combinations of descriptors and ML models have been studied. The results are shown in Fig. 7. The same dataset was applied to all ML models. It was built by randomly selecting and dividing the original dataset into 80% for training and 20% for testing purposes. One can

see in Fig. 7 that the combination of the SOAP descriptor with the NN performed best, with a mean absolute error (MAE) of only about 0.26eV. On the other hand the combination of the ACSF descriptor with the decision tree performed worse with a MAE of almost 0.4eV. However, note that all variants result in a reasonable prediction which can be considered as sufficiently accurate for on-the-fly predictions of formation energies, particularly with a kinetic Monte Carlo description to simulate the oxidation and annealing process.

3.2 Prediction of Defect Structures

The present section introduces the ML based approach to predict the structures of defects in atomistic structures. As in the previous development, the target implementation is the study of hydroxyl E' center defects in amorphous SiO₂ structures. The objective is to produce structures as similar as possible as those obtained by DFT relaxation, while drastically reducing the computational costs.

The proposed workflow is presented in Fig 8, which consists of three steps

- 1) <u>Prediction:</u> Representation of the local environment of the region of interest with a descriptor within the defect free structure; Using this descriptor as an input to a ML model to predict the descriptor of the resulting defect structure.
- 2) <u>Optimization:</u> Using an optimization method to adjust the positions of the atoms in the defect free structure until its descriptor matches the descriptor predicted by the ML model for the defect structure. Therefore, at the end of this step, a ML predicted defect structure is produced.
- 3) <u>Validation</u>: The final step of the process is validating the results. This is done by comparing the ML predicted defect structure with the equivalent target structure produced by DFT relaxation. This is only possible for those structures included in the training and/or testing data set. The validation measure is the descriptor for both structures around the defect site using a mean square error measure.



Figure 8: Proposed workflow to predict the structure of defects in atomistic structures. First, the local environment around the atom of interest in the defect free structure is represented by a descriptor. This descriptor is used within a ML model to predict the descriptor of the defect structure. Subsequent optimization adjusts the positions of the atoms in the defect free structure until their descriptor matches the descriptor predicted with the ML model.

An example of such a prediction and optimization process is shown in Fig. 9. It shows the initial defect free SiO_2 structure (left), the machine learning predicted defect structure (center) and the equivalent DFT-relaxed structure (right). Furthermore, it shows the optimization phase as the difference between the ML predicted structure and the DFT-relaxed structure as the optimization process progresses (measured as the mean squared error between the SOAP

description of the local environment around the defect in the ML predicted structure and the DFT-relaxed structure). The whole optimization procedure was done in 0.46s.



Figure 9: Example of a prediction and optimization process. The final structure was predicted within one second.

As a final measure we have used the average geometrical distance per atom within the region of interest between the ML predictions and the DFT relaxed structures. In total 50 structures

have been randomly selected and analyzed, see Fig. 10. One can see are well within 1Å difference between the two methods (with a mean value of around 0.25Å), which proves the reliable accuracy and robustness of the developed approach.



Figure 10. Benchmark of 50 ML predicted structures vs. DFT relaxed models. The graph shows the average geometrical distance per atom within the region of interest.

Conclusions

We have presented a multitude of atomistic simulation results. First, we used a multiscale approach to identify the various steps of oxidation, starting from the initial phase of O_2 chemisorption on the reconstructed Si(100) surface to the subsequent coverage of the first layer and the various configurations up to the amorphization phase of several layers including the development of the Si/SiO₂ interface. Further studies will be conducted on individual important reactions using DFT, such as the implications of different oxidation states of silicon across the oxidation process. However, the established results already provide detailed insight into the oxidation mechanisms and aid the reaction catalogue for WP5.1 and the developed kMC tool.

Additionally, a broad and detailed defect study on the most prominent candidates in bulk SiO2 has been conducted. We have identified fundamental characteristics such as their formation energies and charge transition levels covering a broad range of defect configurations. These results will directly be used in WP6 and the TCAD simulations to predict the behavior of the electronic devices. In the next step, additional simulations will reveal activation and transformation barriers of defect candidates by using nudged elastic band simulations within our DFT setup. Additionally, the interaction of hydrogen with the pristine and defective SiO₂ network will be investigated. However, due to the computational expenses of these calculations, only a reduced data set will be investigated.

Furthermore, we have developed a machine learning framework which is able to predict the electronic and structural properties of defects with the amorphous SiO_2 network. The promising results will be further extended and a possible application in WP5.1 will be investigated.

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