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Modeling Unconventional Nanoscaled Device FABrication

D5.6: Final KMC models for defect formation

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Introduction

This deliverable presents the outcomes achieved through the utilization of an off-lattice kinetic Monte Carlo (KMC) methodology for investigating the oxidation process of silicon. Our deliberate choice to emphasize the accurate and precise depiction of silicon oxidation chemistry, notwithstanding the associated trade-off in computational efficiency, is justified by the meticulous and comprehensive database compiled by the TUW research team, as expounded upon in deliverables D5.2 and D5.4. The integration of off-lattice KMC with the TUW database establishes a crucial dataset, akin to a comprehensive database, that can be employed as input for TCAD tools based on a lattice-based KMC formalism. The LAAS methodology offers a valuable means to identify defects that arise during growth processes, while *ab initio* calculations performed by TUW enable the characterization of these defects. By employing this combined approach, a direct link can be established between the growth process and the resulting electronic properties.

In this deliverable, we report the results obtained on the simulation of silicon oxide growth from a bare silicon substrate using an off-lattice kinetic Monte Carlo methodology. This simulation is conducted by adsorbing one by one the oxygen molecules on the surface until the formation of an oxide layer of four oxidized monolayers from the topmost layer of the silicon substrate. For thicker oxides, we refer to deliverable D5.4 presenting a complete database of defects formed in thick oxides.

In the first part, we describe the methodological approach used (see also deliverable D5.3). In a second part, we detail the process according to energetic aspects both in energy reaction *i.e.* energy gain and activation barriers at the first reaction's steps and then once the first layer is oxidized. Finally, we perform a chemical analysis of the formed layer and an identification of the formed defects.

1 Topological on-the-fly off-lattice kinetic Monte Carlo

As previously stated and substantiated in deliverable D5.3, due to the intricate nature of the growth process and the amorphous structure of the growing oxide, we opted for Monte Carlo and off-lattice simulation techniques to simulate the growth of SiO_2 from a bare substrate of silicon. In this investigation, we employed the kinetic Activation Relaxation Technique (kART) [1] methodology, which is an on-the-fly KMC approach based on topological considerations. This methodology facilitates the exploration of new atomistic events, even without prior knowledge of the specific events included in the event catalogue, as long as the oxide continues to grow.

In the Monte Carlo (MC) algorithm, an event is selected randomly from a list of potential events, with the probability of choosing an event being proportional to its Boltzmann weight (Figure 1). Each event consists of an initial state, a transition state, and a final state. The Boltzmann weight of an event is given by the expression: $e^{\frac{-E_{bi}}{k_B T}}$ where E_b represents the energy barrier, which is the energy difference between the initial and transition states. The probability p_i of selecting the i^{th} event can be calculated as follows:

$$p_i = \frac{e^{\frac{-E_{bi}}{k_B T}}}{Z} \quad \text{with} \quad Z = \sum_j^{possible} e^{\frac{-E_{bj}}{k_B T}}$$

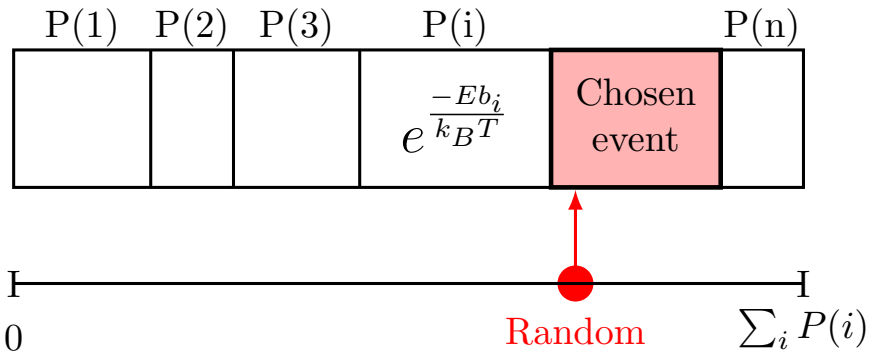
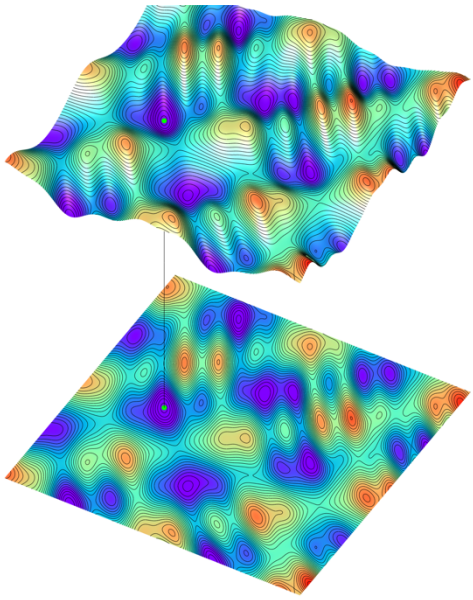


Figure 1: Methodology used to choose one event among the library of possible events.

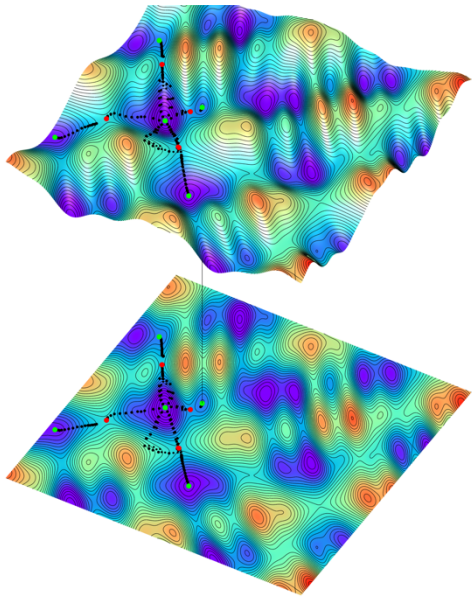
The chosen algorithm is a KMC because once an atomic event is selected, it is applied to the simulation box in order to drive the evolution of the structure. This process is repeated until the stopping criteria of the KMC are met, such as reaching the maximum number of steps or the maximum simulation time.

To determine the simulation time, the transition rate Γ from one configuration to another is computed using the principles of transition state theory [2]. This theory relies on the knowledge of the energy barrier E_b and the phonon frequencies associated with the system. The ratio between the initial configuration and of the transition state phonon frequencies is chosen as a constant commonly equal to $\omega_{vib} = 10^{13}$ Hz [3], known as a conventional attempt frequency for the transitions to occur in solids.

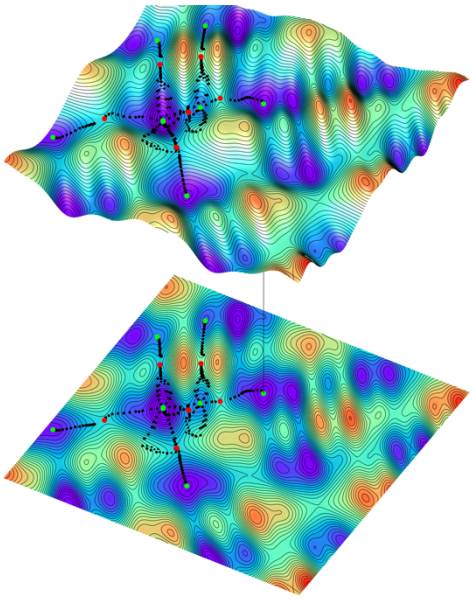
The KMC employed in this study is referred to as "on-the-fly" because the kinetic evolution of the structure can occasionally lead to new atomic configurations that have not been encountered previously. Consequently, at these steps, there are no events in the event library that initiate from the corresponding atomic structure, except for the reverse event that led to it. To address this issue, the event library is updated at each of these KMC steps using the activation relaxation technique (ART). ART, a methodology for energy path exploration, allows for the exploration of the potential energy surface until all the relevant atomic events starting from the newly encountered structure are identified and included in the event library (Figure 2 and Figure 3).



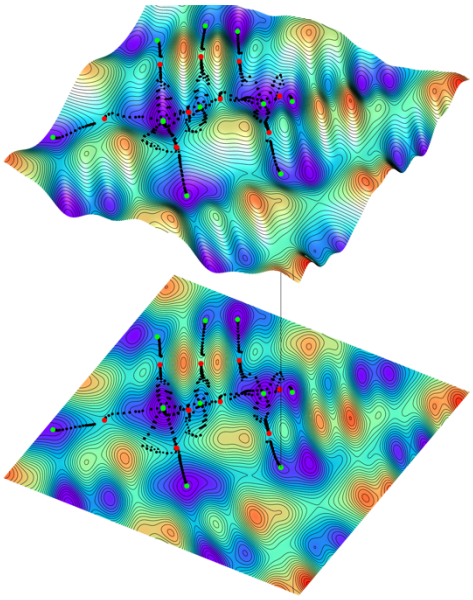
(a) KMC step 1: starting from a relaxed configuration. Min1



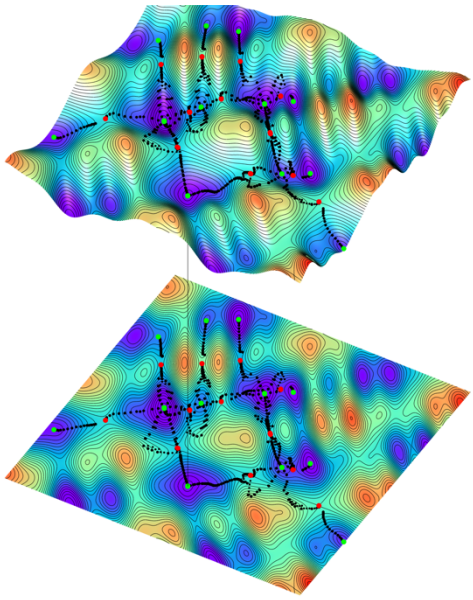
(b) KMC step 2: determination of all the events to escape from the initial configuration. Here, 4 paths are explored and one is selected, which becomes the new configuration to escape (Min2).



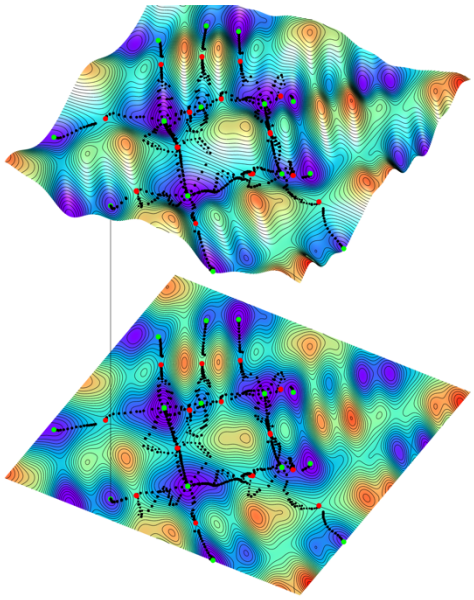
(c) KMC step 3: determination of all the events to escape from Min2. Here, 3 paths are explored and one is selected, which becomes the new configuration to escape (Min3).



(d) KMC step 4: determination of all the events to escape from Min3. Here, 4 paths are explored and one is selected, which becomes the new configuration to escape (Min4)



(e) KMC step 5: determination of all the events to escape from Min4. Here, 4 paths are explored and one is selected, which becomes the new configuration to escape (Min5).



(f) KMC step 6: determination of all the events to escape from Min5. Here, 4 paths are explored and one is selected, which becomes the new configuration to escape (Min6)

Figure 2: Exploration of the energetic landscape from minima to minima (green dots) by finding all the saddle points (in red) thanks to kinetic ART methodology each black dot represents a force calculation.

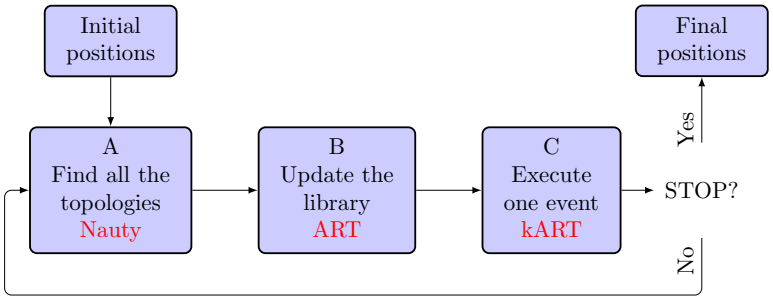


Figure 3: General Algorithm for an on-the-fly topologic kinetic Monte Carlo.

This KMC approach can be categorized as topological because it only stores a small number of atomic positions in each triplet of initial-transition-final structures that define an event. Specifically, it focuses on the atomic positions within a topological radius centred on the atom undergoing the most significant movement. By adopting this approach, not only is memory space conserved, but events can also be assigned to multiple atoms within the simulation box that share the same topology. For instance, the event corresponding to the diffusion of single oxygen atoms into bulk silicon can be applied to all oxygen atoms within the box that exhibit the same topology. This advantageous feature eliminates the need to re-explore the corresponding potential energy surface (PES) when recognized topologies already exist in the event library.

Furthermore, this KMC methodology is considered off-lattice, in contrast to other KMC methods, due to the study's focus on the emergence of new topologies that are not confined to well-defined crystalline or defect sites. In the case of SiO_2, which is amorphous, this off-lattice approach is particularly relevant.

2 Details of the simulations

2.1 Simulation box

The initial simulation box consists of 1200 silicon (Si) atoms arranged in their crystalline diamond-like positions, distributed across 24 layers with 50 atoms in each layer, as depicted in Figure 4. The first O_2 molecule has been deposited in the system. To emulate bulk properties, the positions of the bottom four layers are kept fixed. To simulate the surface and avoid interactions resulting from periodic boundary conditions, an empty space of 50 Å is included above the top layer.

To achieve surface reconstruction, a molecular dynamics simulation was performed by heating the simulation box to 700 K during 10 ps using the code LAMMPS. A reactive force field, both for the surface preparation and for the oxidation part discussed in the next section is used. This process led to the well-known dimer-like reconstruction of the Si (100) surface, as illustrated in Figure 5. It should be noted that due to the heating simulation, the dimers do not form a periodic structure characterized by alternating dimer rows and channels.

The chosen simulation box is sufficiently large to minimize the mechanical stress induced by the creation of the oxide. This is crucial when studying interfaces, as the substrate can impose its cell parameters on the deposited layers, often resulting in significant stress at the interface. However, in the case of SiO_2 deposition, which is amorphous, the stress-induced effects are small compared to crystalline deposition.

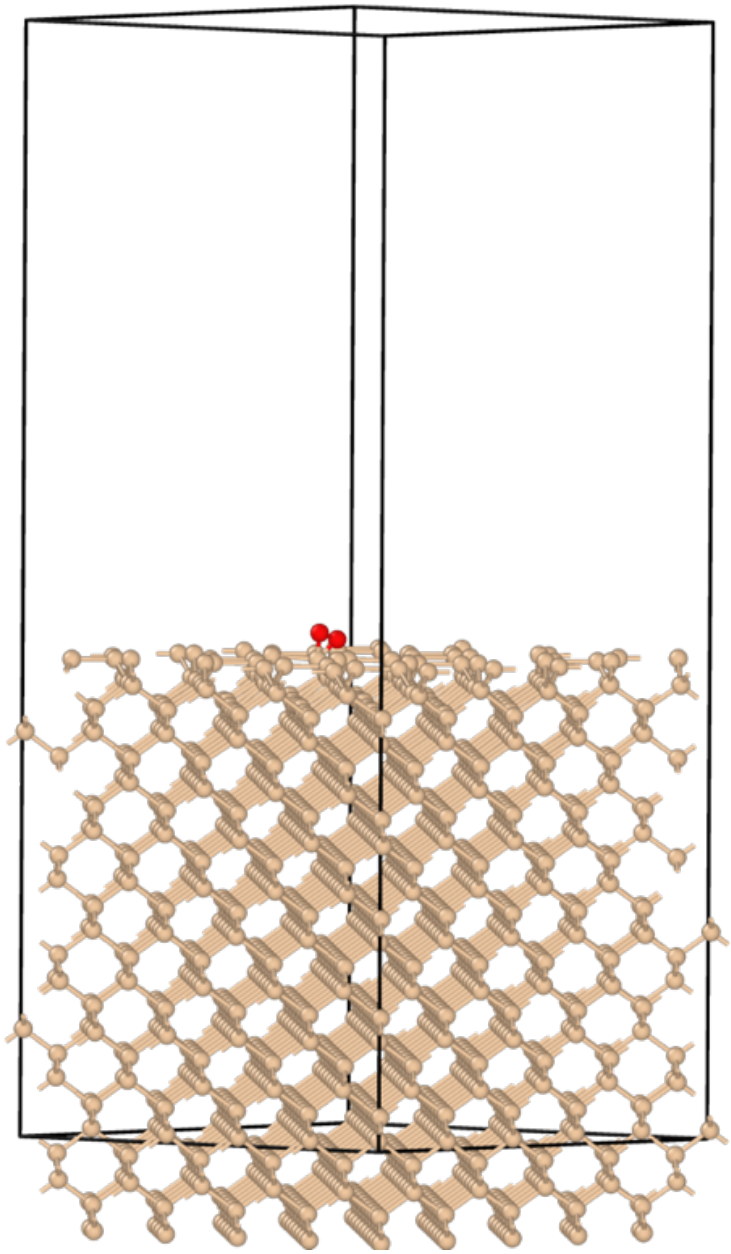


Figure 4: Simulation box consisting of 1200 silicon atoms in beige. Oxygen atoms are in red. this colour code is used throughout the deliverable.

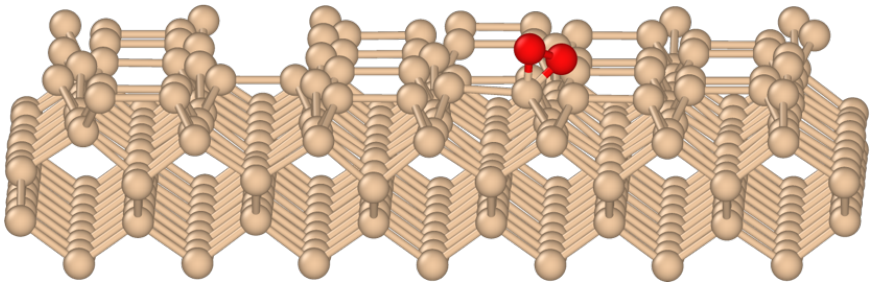


Figure 5: Si(001)-(2x1) reconstruction of the silicon surface obtained after heating simulation at 700 K of a silicon bare substrate using Molecular Dynamics simulation.

2.2 Choice of the interatomic potential

The selected potential for this study is the reactive force field (reaxFF), as described in the work by Nayır *et al.* [4]. The reaxFF potential is capable of accurately representing the interactions between silicon (Si), oxygen (O), and hydrogen (H) atoms. This potential incorporates the reactive nature of chemical reactions, allowing for a comprehensive description of the Si/O/H system in the simulation.

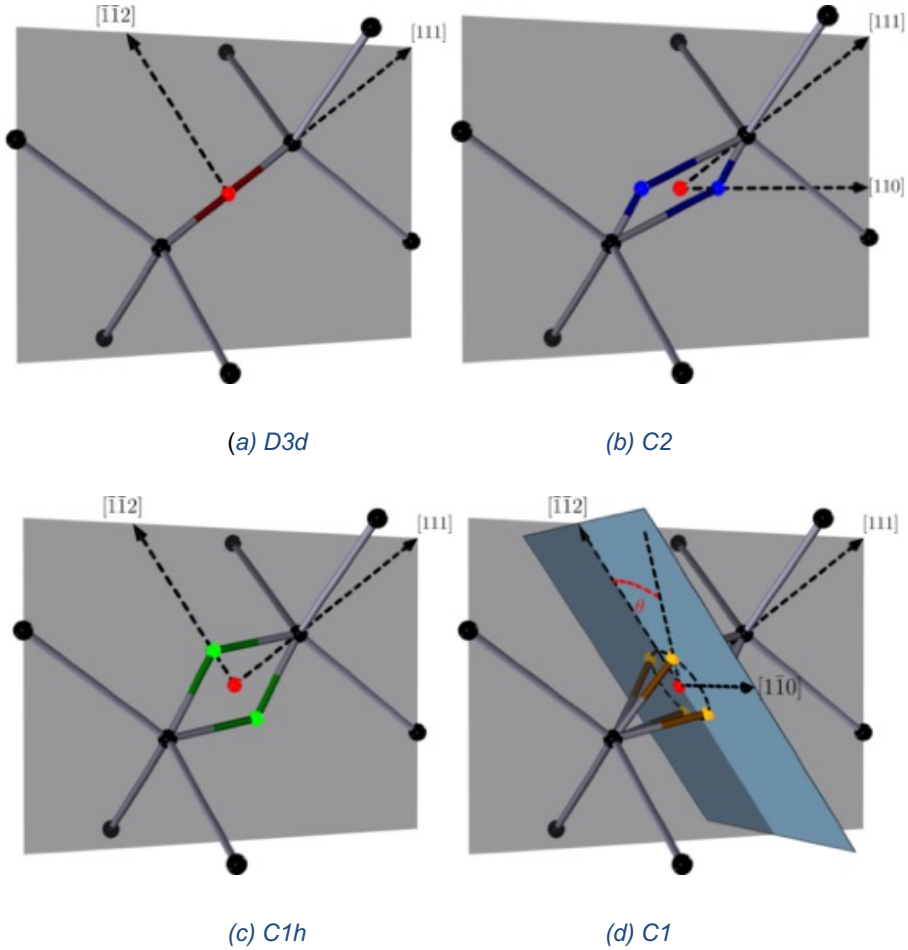
The validity of the simulation is intrinsically reliant on the quality of the employed potential. As we will explore subsequently, the conducted Kinetic Monte Carlo simulations are intricate and computationally extensive. Our focus has been on utilizing a singular potential that allows us to elucidate the obtained outcomes. Nevertheless, within this study, we have also initiated oxidation simulations employing the potential developed by the TUW research team. This potential has been meticulously calibrated using a vast dataset, and we anticipate it will provide a more accurate representation of the chemical processes and growth reactions occurring in the oxide. Presently, this work remains ongoing.

2.3 Oxygen behaviour: adsorption, topology, local minima

To simulate the deposition of O_2 molecules, they are sequentially added to the system, 3 Å above the surface, at random locations and with random angles (as shown in red in Figure 4). The atomic positions are initially relaxed, followed by a few steps of kART simulation until the total energy of the system stabilizes and no longer decreases. At this point, kART is automatically paused and restarted with a new O_2 molecule added. This choice is done in order to reduce the simulation time, which is a constraining factor when utilizing a off-lattice KMC. A new O2 molecule is introduced immediately after the oxygen atoms from the preceding molecule have been inserted into the Si-Si bonds. During the initial phases of the simulation, it is assumed that surface reactions between O_2 and Si occur rapidly.

To define the topology of each central atom, a connectivity graph is constructed by considering all atoms within a radius of 6 Å from the central atom. For each new topology, more than 30 explorations of its potential energy surface are performed using ARTn, employing random deformations centred around the central atom.

During the exploration of the PES with ART, it is crucial to initiate the displacement with a norm (magnitude) of at least 0.7 Å to avoid getting trapped in closely located local minima. These local minima are attributed to changes in Si-O-Si angles that do not require energy, as they do not break a bond, resulting in a large number of metastable positions. An example of such metastable positions is illustrated in Figure 6, showcasing the case of an oxygen atom in bulk silicon. In the KMC simulation, it is crucial to avoid the occurrence of such nano-events that do not contribute to the system's evolution. These events can introduce unnecessary noise to the simulation and result in extended computational times.



(a) D3d (b) C2

(c) C1h (d) C1

Figure 6: Summary of all the metastable atomic positions known for one oxygen atom (red, blue, green and orange balls) between two silicon atoms (black balls). Corresponding symmetry groups are given.

The kinetic Monte Carlo simulation of silicon oxidation is performed at a temperature of 700 K. The occurrence of each diffusion event is contingent upon this specific temperature, and the computational algorithm yields a simulated time that represents the duration of residence before a subsequent reaction takes place at the given temperature. Consequently, this information allows for the determination of the overall duration of the oxidation process.

3 Results: Analysis of the simulation

3.1 Topologies and events

In this paragraph, we present the complexity of the studied system by detailing the number of encountered topologies as the simulation progresses. After 250 KMC steps, i.e., 250 applications of events (adsorption and diffusion), the system has already explored 20000 different topologies (as shown as “ever seen” in the bottom part of the Figure 7). Each of these topologies can be further explored and searched for events, which represents a considerable number to analyse.

Due to computational cost considerations, we do not analyse all of these topologies. Only a subset is selected ("explored with ARTn" in the top part of the Figure 7), particularly those centred on oxygen atoms, to initiate explorations using the ART method. Among these selected topologies of interest (approximately 1500 topologies after 250 KMC steps), 20 diffusion path searches are performed (resulting in 3000 searches per KMC step at this stage of the simulation), yielding an average of 10 new events (initial configuration, final configuration, and barrier) per active topology. Consequently, new topologies are generated for exploration in the next step. These selected events are then added to the library.

However, at any given time, not all topologies are active, as the system evolves, configurations change, and some topologies disappear while others emerge (Figure 8). For those which appear if it does not exist in the library of events, there is a search with ARTn, and if it does exist, it is taken directly from the library which is stored.

At each KMC step, we only have a subset of active topologies, approximately 800 possible events at each step. Out of the 800 events available, the system will evolve during growth by selecting one event using the Monte Carlo algorithm, choosing an event based on its associated rates or probabilities, allowing the system to undergo a transition from its current state to a new state. This selection process ensures that the evolution of the system follows the principles of statistical mechanics and captures the dynamics of the growth process.

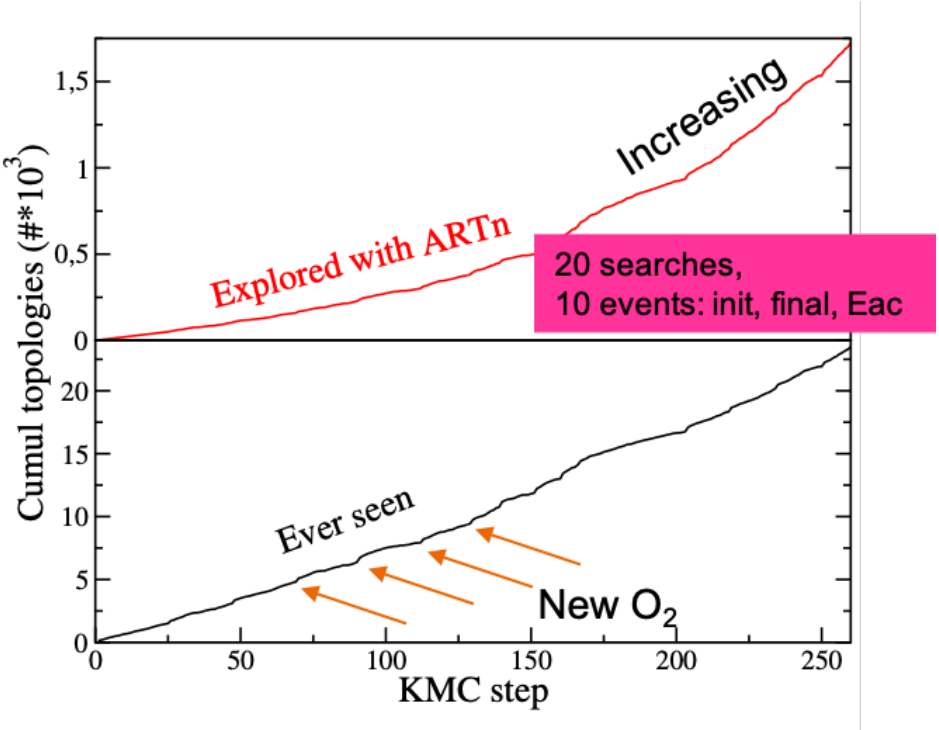


Figure 7: Number of topologies encountered in the KMC simulation and number of topologies explored by ART as a function of simulation progress in number of KMC steps.

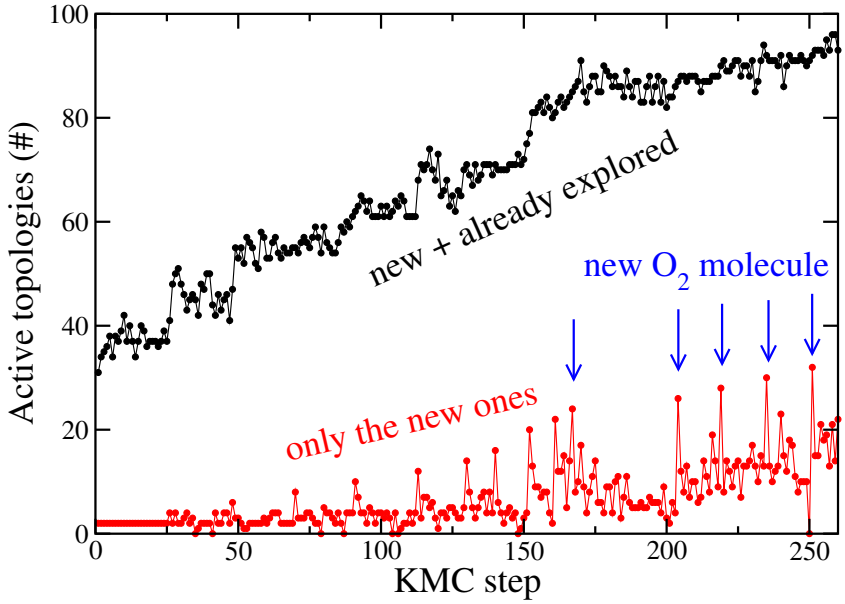


Figure 8: Identification of active topologies during KMC simulation.

The Figure 9 illustrates the events that were calculated to demonstrate the code's capability to explore a wide range of diffusions and other mechanisms. It is important to note that not all events are necessarily selected to be included in the catalogue.

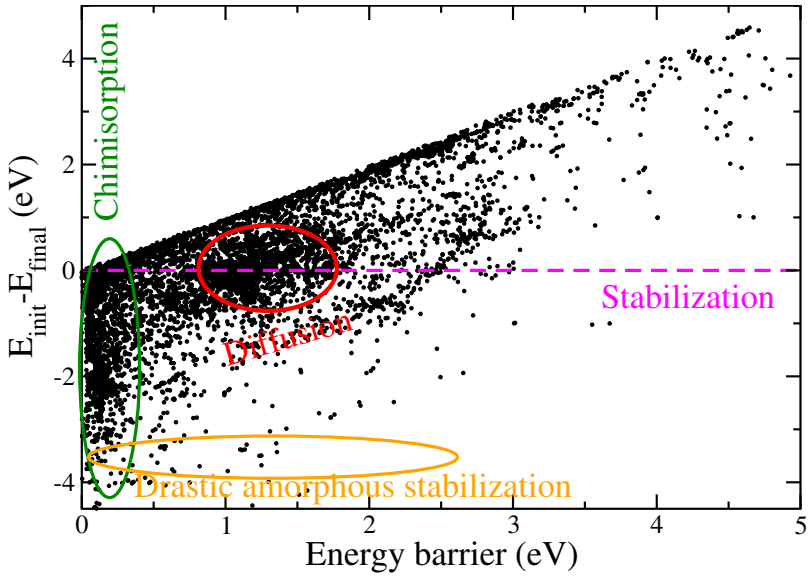


Figure 9: Illustration of the diversity of mechanisms encountered in the KMC simulation

3.2 Energetics

From these simulations, various analyses can be conducted.

One analysis involves examining the total energy of the system in Figure 10. It is observed that when adding a molecule, the energy of the system experiences significant fluctuations. However, for the remaining events, the energy variations are relatively small. This behaviour aligns with observations in films, where initial stabilization involves several small movements, followed by limited energy fluctuations as oxidation progresses.

The simulation provides valuable data for studying growth, including the analysis of energetic barriers to apply an event (Figure 11). At each step of the simulation, energy barrier values can be obtained, offering insights into the energetic requirements for different events. Additionally, the ranges of activation barriers encountered throughout the simulation can be observed, providing further information about the energetic landscape of the system. These findings contribute to a comprehensive understanding of the growth process.

By analysing the obtained data, it is possible to categorize the observed events into distinct families of mechanisms based on their associated activation barriers. This categorization helps in understanding the underlying processes and mechanisms involved in the system's behaviour.

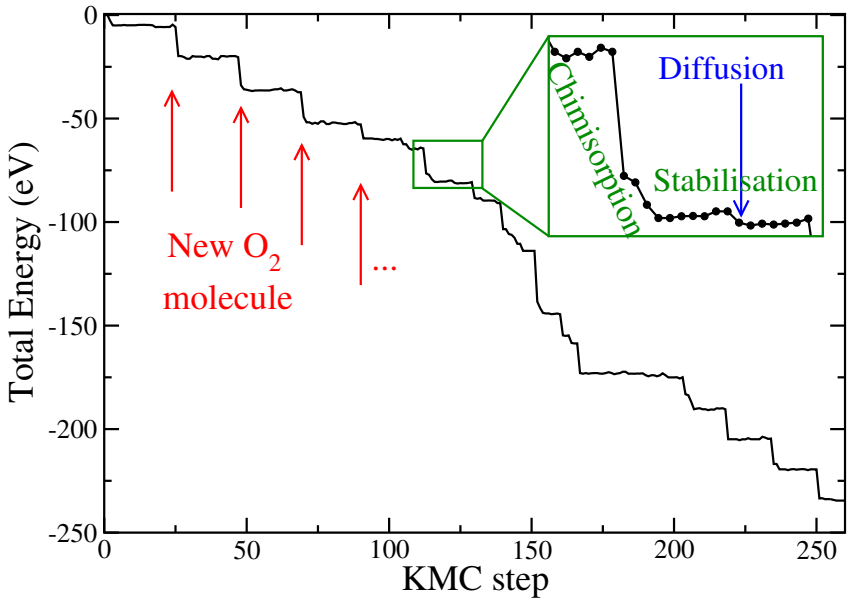


Figure 10: Evolution of the total energy of the system as a function of simulation progress in number of KMC steps.

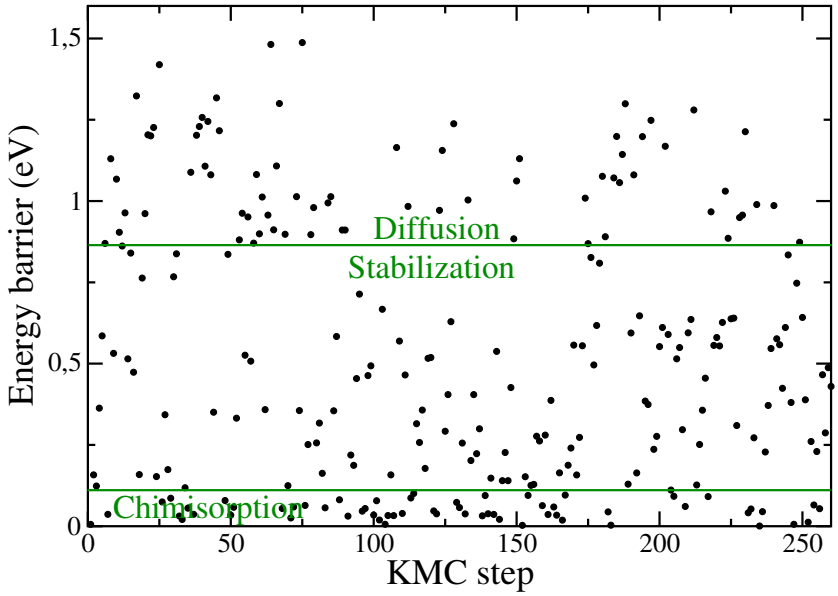


Figure 11: The simulation results allow for the identification of ranges of activation barriers and their allocation to different families of mechanisms encountered during the simulation.

In the KMC simulations, specific features of each event can be identified (Figure 12). Notably, it can be observed that certain events exhibit low activation barriers, which are attributed to processes such as chemisorption and dissociation of O_2. These events contribute energy to the system.

On the other hand, a significant number of events are associated with larger activation barriers, typically around 1-1.5 eV. These events correspond to the diffusion of individual O atoms within the system. Despite the higher energy requirements, these diffusion events play a crucial role in the growth process.

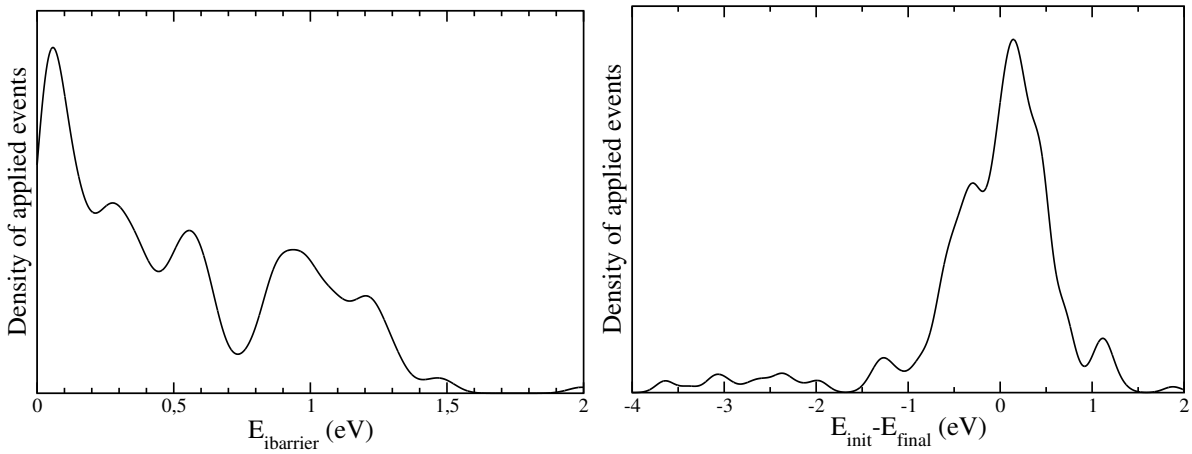


Figure 12: The simulation results allow for the identification of ranges of activation barriers and their allocation to different families of mechanisms encountered during the simulation.

3.3 Chemistry

Figure 13 illustrates the atomic structure of the silicon oxide layers obtained through the growth process, where oxygen molecules are added one by one onto the silicon surface. The figures provide a visual representation of the arrangement and bonding of atoms within the silicon oxide layers. By examining the atomic structure, important information about the spatial distribution, connectivity, and organization of the silicon and oxygen atoms can be gleaned, aiding in the understanding of the oxide layer's properties and its impact on the overall system.

The simulation provides insights into the increase in volume of the silicon substrate resulting from the formation of the oxide layer. In our simulation, the surface area is 26.13 x 26.13 $Å^2$. After oxidizing three silicon monolayers (Figure 13 (b)), we observe an average increase in the substrate thickness of approximately 1.43 Å. This corresponds to an increase of 11.35 $Å^3$ per oxygen atom.

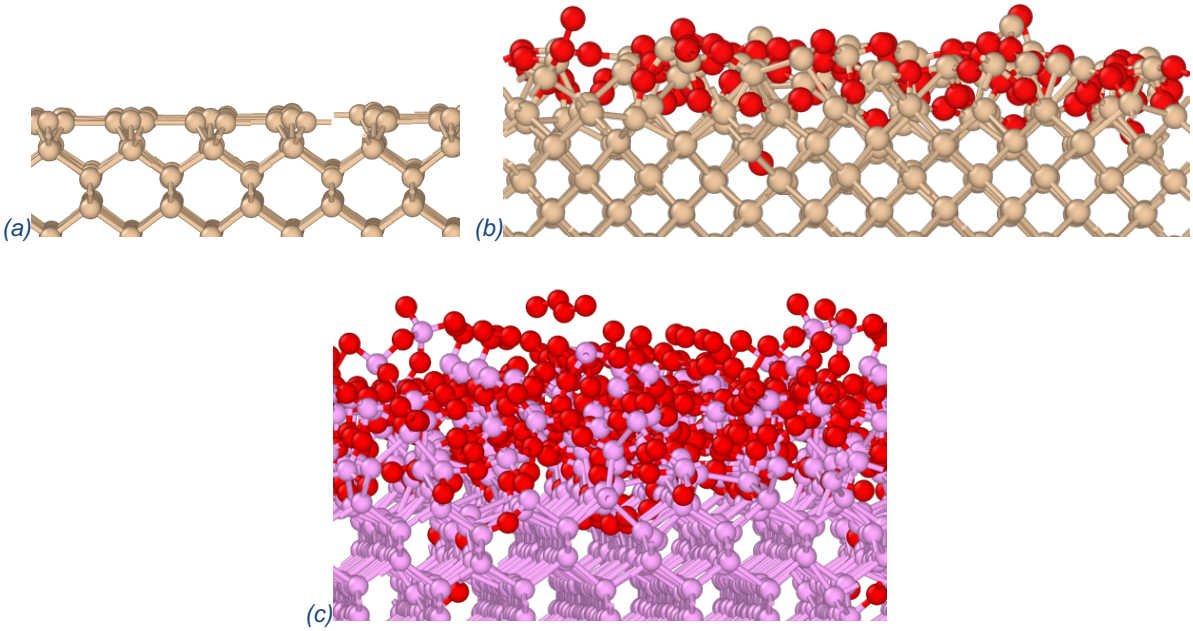


Figure 13: Representation of the atomic structure of the (a) silicon substrate, and (b) and (c) of two silicon oxide thicknesses obtained by KMC simulation.

Analysing the atomic structure depicted in Figure 13 allows for the determination of various structural parameters, such as average distances between silicon (Si) and oxygen (O) atoms within the oxide layer. This analysis provides valuable insights into the bonding and coordination of Si and O atoms, shedding light on the chemical interactions and stability of the oxide layer (see Figure 14). Additionally, the analysis of the atomic structure enables the calculation of Si-O-Si and O-Si-Si angles, which characterize the geometric arrangement of atoms within the oxide layer. These angles provide information about the local bonding environment and the spatial orientation of Si and O atoms. Close to the interface between the silicon substrate and the oxide layer, the analysis can reveal specific Si-O-Si and O-Si-Si angles that play a crucial role in determining the properties and behaviour of the interface region. Understanding these angles at the interface is particularly important for studying interfacial reactions, charge transfer, and overall interface stability.

In the following KMC step, the angles and distances that deviate from the mean values will undergo stabilization. These variations from the average values indicate potential structural distortions or instabilities within the system. The stabilization process aims to restore these angles and distances towards their equilibrium positions, promoting a more energetically favourable configuration. By addressing these deviations, the system can achieve a more stable and balanced state, facilitating the progression of the KMC simulation.

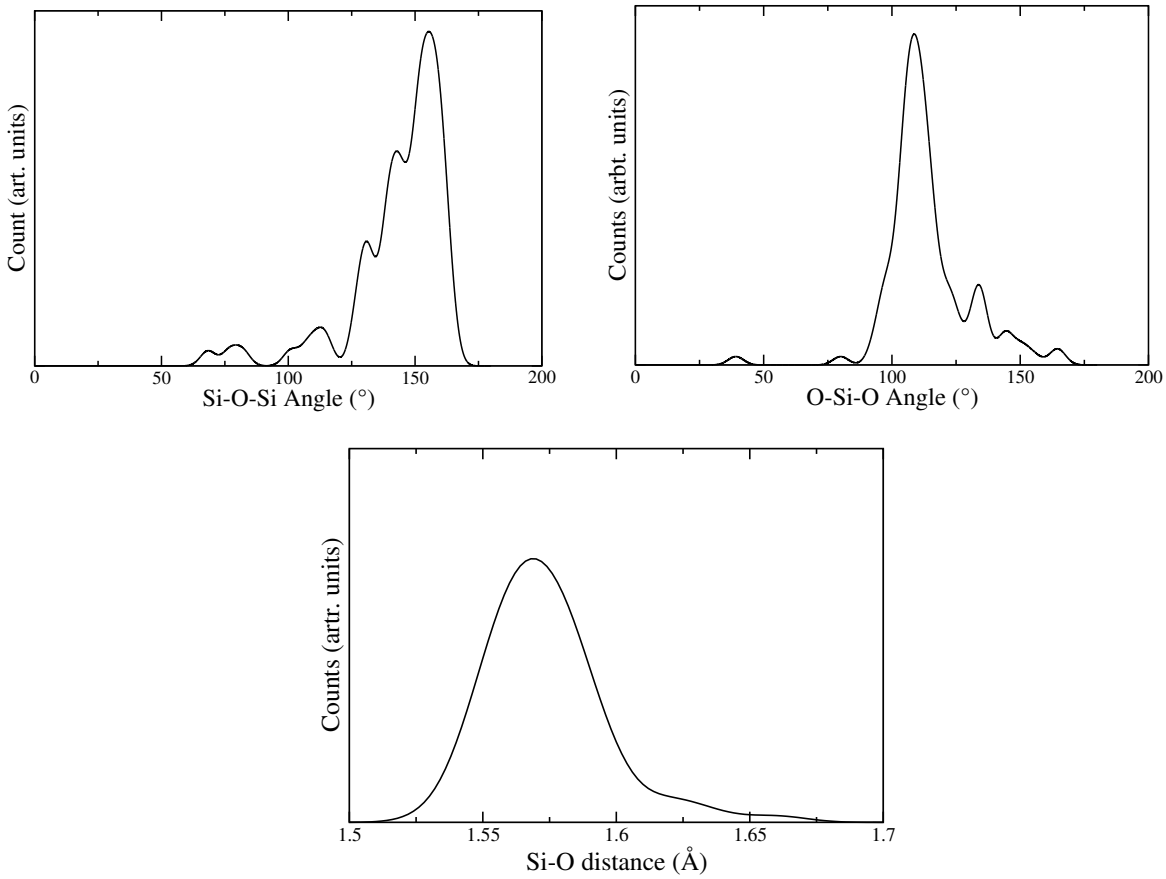
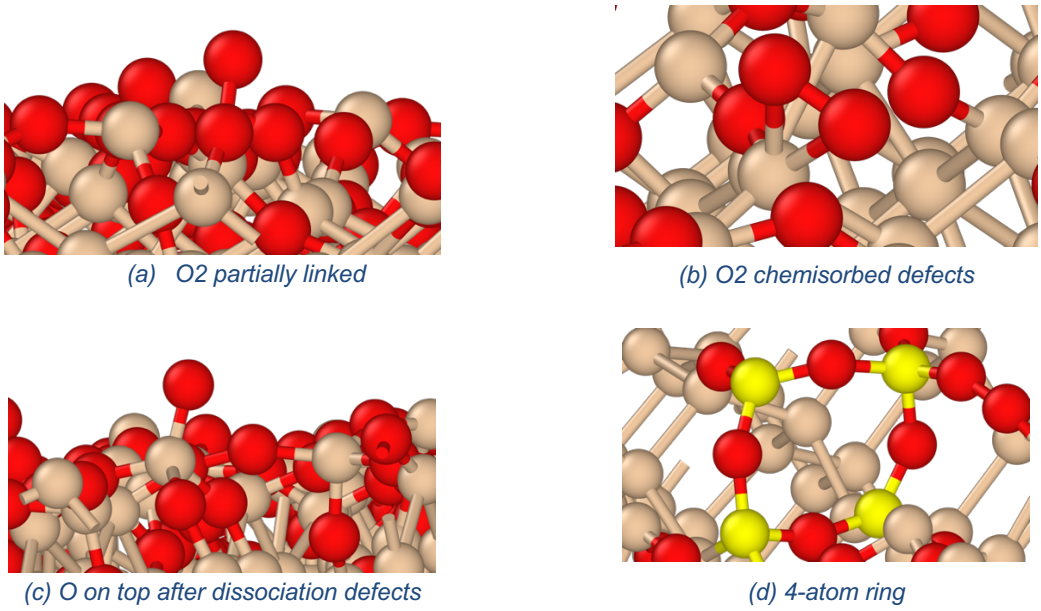


Figure 14: Analysis of the microstructure (bond angles and bond lengths) of the oxide layer obtained after simulation of silicon oxidation by KMC.

3.4 Identification of structural defects

The ultimate goal of KMC simulations is to identify the structural defects formed during the oxide growth and determine when they occur. In order to discover defects, we have characterized the simulated oxide layer. The defects observed for an oxidation of 3 silicon monolayers are presented in Figure 15.

Within this oxide layer, several types of defects have been identified, including O_2 partially linked defects, O_2 chemisorbed defects, O on top after dissociation defects, and 4-atom ring defects. These defects represent deviations from the ideal atomic arrangement and can significantly impact the properties and performance of the oxide layer. To establish definitively this link, the KMC simulated oxide layer will be provided to the TUW team.



(a) O2 partially linked

(b) O2 chemisorbed defects

(c) O on top after dissociation defects

(d) 4-atom ring

Figure 15: Structural defects identified in the 3 monolayers silicon oxide simulated using KMC approach.

Summary and conclusions

The off-lattice KMC code employed in this study is highly capable in depicting the step-by-step evolution of matter towards an amorphous state. However, it is important to acknowledge the significant computational expenses associated with this approach (Figure 16). As a result, its current state of development does not make it a directly viable tool for industrial applications, as is the case with TCAD codes. The computational demands of the off-lattice KMC code hinder its practical implementation on an industrial scale. Nonetheless, ongoing advancements and optimizations in computational algorithms and hardware may pave the way for future developments, making it a more accessible and efficient tool for industrial applications.

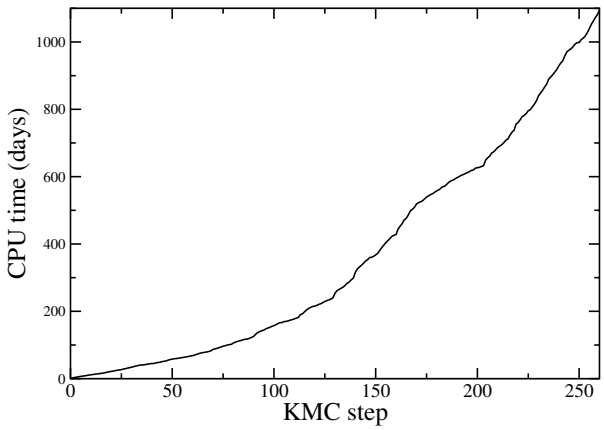


Figure 16: Simulation time.

In this study, we have effectively demonstrated the advantages of utilizing an off-lattice Kinetic Monte Carlo (KMC) code to simulate the oxidation of silicon. Our research has yielded several significant contributions:

- Through the analysis of the different topologies, our primary objective is to identify the more prevalent configurations that play a crucial role in the growth process and potentially contribute to defect formation.
- by scrutinizing the distribution and range of activation barriers within each family of mechanisms, we have gained valuable insights into the energetic requirements and relative probabilities of different pathways and reactions during the simulation. This knowledge enhances the understanding of the dynamics of the system and the underlying mechanisms governing the growth process.
- The detailed examination of each event, including their associated activation barriers, has provided valuable insights into the energetics and mechanisms that drive the behavior of the system during the simulation. This analysis has shed light on the intricate interplay between processes such as chemisorption, dissociation, and diffusion, and their influence on the growth dynamics.
- By looking at the structural parameters, we have acquired valuable insights into the atomic-level characteristics of the silicon oxide layers. This deeper understanding of the oxide formation process and its impact on material properties has significant implications for the stability, reliability, and functionality of the oxide layer.
- The identification and comprehensive analysis of these defects have provided valuable insights into the mechanisms and kinetics governing defect formation during oxide growth. This knowledge is instrumental in comprehending the stability, reliability, and functionality of the oxide layer, while also guiding the refinement of growth processes and the advancement of materials for various applications.

The ongoing work aims at further investigating the growth process by forming a thicker oxide layer. Additionally, collaboration with TUW has been initiated to compare the defects formed in the KMC simulations with *ab initio* calculations. This collaborative effort seeks to establish a connection between the structures formed during growth and their impact on the electronic properties of the oxide layer. By combining the insights from both simulation and theoretical calculations, a comprehensive understanding of the structural and electronic characteristics of the oxide layer can be achieved, leading to further advancements in the field.

As a continuation of this work, it is certainly pertinent to conduct a similar study at a different temperature to explore the influence of temperature on the quality of the oxide layer achieved. To facilitate a statistical analysis, it will also be imperative to perform multiple simulations at a specific temperature. For these statistical studies, we now have a catalogue of KMC events available. The KMC catalogue generated from our already performed simulations will be used as input for our future simulations (such as different surfaces or temperatures), aiming to reduce the associated simulation time.

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