A Molecular Dynamics Approach to Studying Gate Oxides in Ge-MOSFETs

by

Amirsalar Heydari Haratameh

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A Molecular Dynamics Approach to Studying Gate Oxides in Ge-MOSFETs

submitted by **Amirsalar Heydari Haratameh** in partial fulfillment of the requirements for the degree of **Master of Applied Science** in **Electrical and Computer Engineering**.

Examining Committee:

André Ivanov, Electrical and Computer Engineering *Supervisor*

Peyman Servati, Electrical and Computer Engineering *University Examiner*

Abstract

As silicon-based transistors are reaching their performance limit, a growing need for a new semiconductor material has arisen. Germanium has been suggested as the potential substitute for silicon-based Metal-Oxide-Semiconductor Field-Effect Transistors (MOSFETs). This dissertation is focused on the source of reliability issues of MOSFETs fabricated on germanium and offers several solutions to cope with MOSFETs reliability issues. Due to the miniaturization of electronic devices, especially MOSFETs, some reliability challenges have arisen, such as the higher threshold voltage and increased gate leakage current. This device downscaling has led to a poor interface quality at the dielectric/substrate interface of Ge-MOSFETs. I employed Molecular Dynamics (MD) tools to investigate the nature of the dielectric material structure on the germanium substrate and the type of defects responsible for electrical degradation. This dissertation is dedicated to proposing several solutions which enable the semiconductor industry to mitigate the associated reliability issues of Ge-MOSFETs which leave behind the commercialization of these MOSFETs. A reactive molecular dynamics force field was employed in this research, enabling the simulation of ongoing bond breaking and formation. In addition to finding the effect of oxidation temperature on the density of interfacial defects, this research has shed light on the effect of oxide thickness on interface quality. The need for stabilizing the native oxide of germanium leads to proposing a novel approach to improve both interface quality and dielectric constant. Dilute concentrations of aluminum were doped into the oxide network, and as a result, improved dielectric constant and enhanced dielectric/substrate interface quality were obtained.

Lay Summary

As a contribution to replacing the current widely-used silicon-based Metal-Oxide-Semiconductor Field-Effect Transistors (MOSFETs) with germanium-based ones which offer higher electron and hole mobility, with lower power consumption, and higher speed - this work proposes several solutions to improve the MOSFETs fabricated on germanium. The current problem with germanium-MOSFETs is that the interface of the dielectric layer, which is located on top of the MOSFETs' channel, is not as high quality as its Si counterparts, resulting in reliability-related challenges (higher threshold voltage and gate leakage current). Through conducting Molecular Dynamics (MD) simulations, the author proposed solutions to stabilize the dielectric layer to reach a better interface quality between the dielectric/body of MOSFETs, while improving the dielectric constant. As a part of the solutions proposed, aluminum was doped into the molecular structure of the dielectric layer.

Preface

The presented research in this dissertation was conducted and written by Amirsalar Heydari under the supervision of Dr. André Ivanov at the System On Chip (SOC) laboratory in Electrical and Computer Engineering department at the University of British Columbia. The simulations were designed by Amirsalar Heydari in collaboration with Dr. Arash Sheikholeslam, the former PhD student in our research group. I analyzed the simulation results and some of the results of this dissertation have been submitted for publication as:

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Acronyms

- **BJT** Bipolar Junction Transistor
- **CN** Coordination Number
- **DFT** Density Functional Theory
- FET Field-Effect Transistor

GROMACS GROningen MAchine for Chemical Simulations

- IC Integrated Circuit
- JFET Junction Field Effect Transistor

LAMMPS Large-scale Atomic/Molecular Massively Parallel Simulator

- MC Monte Carlo
- MCN Mean Coordination Number
- MD Molecular Dynamics
- MOSFET Metal-Oxide-Semiconductor Field-Effect Transistor
- NAMD Nanoscale Molecular Dynamics
- **NPT** Number-Pressure-Temperature
- **NVE** Number-Volume-Energy
- NVT Number-Volume-Temperature

- **PM3** Parameterized Model number 3
- **RDF** Radial Districution Function
- **ReaxFF** Reactive Force Field
- VAP Valance Alteration Pairs

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Chapter 1

Introduction

Research is what I'm doing when I don't know what I'm doing. — Wernher von Braun (1977)

1.1 Historical Review

There is no doubt that transistors have changed the technology world because they are the building blocks of computer hardware. In order to replace the old vacuum tubes, which were large and consumed a considerable amount of power, the very first transistors were fabricated on germanium (Ge) – similar to the first integrated circuits – and invented by William Shockley, John Bardeen, and Walter Brattain, the recipients of Noble Prize in physics [3], in 1947 at Bell laboratories. Transistors are semiconductor devices utilized either for amplifying or controlling the flow of power by acting as a switch. Two main types of transistors are Bipolar Junction Transistor (BJT) and Field-Effect Transistor (FET), which is categorized into Metal-Oxide-Semiconductor Field-Effect Transistor (MOSFET) and Junction Field Effect Transistor (JFET). The MOSFET was patented initially in 1933, but not commercialized until thirty years later, due to the lack of a mature understanding of dielectric/substrate interface [4].

Since then, MOSFETs have been merged into the Integrated Circuit (IC) with an increasing density due to the miniaturization of them. The accommodation of more MOSFETs on ICs has led to higher switching speed and lower costs. In 1965 Gordon E. Moore [5] noticed a trend in the size reduction of transistors by analyzing the number of on-chip transistors. He figured that the number of transistors on an IC is doubled every two years. Today, this is known as Moore's law. For decades, this trend has continued; however, this downscaling has a limit and is about to end [6], as NVIDIA's CEO Jen-Hsun Huang also declared recently ¹. As the MOSFETs shrink in size, their gate oxide becomes thinner and this causes higher gate leakage current due to exceeding the limit for electron tunnelling (2 nm) [6].

1.2 Motivation

Historically, the first MOSFETs were built on germanium (Ge); however, since the dielectric/substrate interface is of higher quality in silicon-MOSFETs compared to Ge counterparts [7, 8], soon, the industry switched to silicon (Si) as the leading semiconductor component of transistors. Silicon's native oxide - silicon dioxide (Silica) - is known to be a more stable oxide than germanium dioxide (Germania) and has a better oxide/substrate interface quality (fewer interface defects). Therefore, this matter made Si a favourable material compared to Ge to be utilized as the main component of MOSFETs. On the other hand, Ge is known to possess a higher electron and hole mobility compared to Si. In transistors, this charge carrier mobility determines how fast the device can switch between on and off state. Germanium has been accounted for having bulk electron and hole mobilities twice and four times those of Si, respectively [6, 9]. In detail, the electron and hole mobility of Ge is 3900 and 1900 cm^2/Vs , respectively [10]. Consequently, Ge has returned to the focal interest of R&D for the future. In particular, Ge generally offers the highest bulk hole mobility among all elements of Groups IV, and III-V combined semiconductor materials. However, the oxide/substrate interface in Ge-MOSFETs is not as high quality as Si-MOSFETs. Although hydrogen passivation is effective for reducing oxide/Si interface defects, it is not highly effective for stabilizing the high-k/Ge interface [6, 11, 12].

Since transistors are being shrunk in size to facilitate charge transport so that faster transistors are produced, transistors speed is dominated by injection velocity

¹https://www.extremetech.com/computing/256558-nvidias-ceo-declares-moores-law-dead

at the source region of MOSFETs. Thus, channels with high mobility are required for the future of nanoelectronics [6]. While possessing the highest hole mobility, Ge bulk electron mobility is less than that of most of the III-V materials, so it is worth studying III-V combined-semiconductor MOSFETs. Nevertheless, since the surface passivation for all III-V materials faces a severe technical issue, it is more straightforward to fabricate MOSFETs on Ge [6, 13, 14].

Moreover, the processing temperature of Ge is lower than Si, so it is easier to use Ge-based MOSFETs with high-k materials [6, 15]. Germanium has a low melting point of 938 °C. This fact eventually facilitates the shallow junctions formation due to the low-temperature activation of source/drain dopants (400 - 600 °C) [6, 16] compared to Si case (1300 °C [8]).

Last but not least, Ge energy band gap ($E_g = 0.66 \text{ eV}$) is lower than that of Si ($E_g = 1.12 \text{ eV}$), enabling the device to work at lower voltages [16]. Consequently, there will be lower power consumption in integrated circuits [17], further V_{DD} scaling [16], and broader absorption of wavelength spectrum [18].

1.3 Metal-Oxide-Semiconductor Field-Effect Transistors

A MOSFET is a four-terminal device consisting of a source and drain terminals, body (substrate), and gate, all of which are depicted in Figure 1.1. Depending on the dopant type of the source, drain, and body there are n-channel and p-channel MOSFETs, which conduct electrons or holes respectively upon applying the voltage on the gate. The metal gate is shielded from the substrate by an insulating layer called the gate dielectric which separates these two terminals. The gate dielectric is an oxide layer which is grown on the substrate by exposing it to an oxidant ambient. The quality of the oxide is a crucial factor in fabricating any type of MOSFETs.

Today, as a part of scaling down electronics, MOSFETs with a shallow dielectric layer are desired because by decreasing the thickness of the dielectric layer, the capacitance of the MOSFET increases (explained in detail in Section 1.5), leading to higher device performance. However, by reducing the thickness of the insulating layer (the dielectric layer), the gate leakage current rises due to the flow of charge carriers through it. The solution to achieving a high-performance MOSFET is using a novel material as the gate oxide with a high dielectric constant, but small



Figure 1.1: Schematic of a MOSFET.

thickness. To serve this purpose, there are some high- κ materials – such as HfO₂, ZrO₂, and Al₂O₃ – previously proposed to be utilized as the dielectric layer. However, due to the intermixing of oxygen atoms with the substrate constituent atoms, it is inevitable to have a native oxide interlayer with lower permittivity between the high- κ layer and substrate [18–20]. Accordingly, this fact supports the necessity for a method to improve the native oxide interface quality at the substrate.

1.4 Germanium MOSFETs and the Current Problems

As mentioned earlier, germanium has several advantages over silicon which has drawn attention to it again. Although Si-MOSFETs are the most abundant transistors, by reaching the fundamental and technical limits in scaling them down, a novel material is needed as a replacement for Si [16] so that the expectations for high-performance ICs are satisfied. However, unlike SiO₂/Si interface, GeO₂ does not possess a high quality interface with the substrates built in Ge. It is been stated that at around 400 °C volatile GeO is formed near the interface of GeO₂/Ge, making the gate oxide thermodynamically unstable [16, 19] and causing reliability issues. It has been reported that the interface state density (D_{it}) of SiO₂/Si is around $2 \times 10^{10} \text{ cm}^{-2}$, while that of high- κ /Ge gate stacks is between 10^{11} to 10^{12} cm^{-2} . High interface state density of Ge MOSFETs causes switching the threshold volt-

age considerably. However, historically, D_{it} values for high- κ /Si were between 10^{11} to $10^{12}cm^{-2}$, much higher than the current state. Hence, this improving trend for Si MOSFETs may enable further reduction of interfacial defects in Ge-based MOSFETs [6].

There have been various suggested methods to reduce the interface state density, including the passivation of the dielectric/substrate active interface (active sites) with a few monolayers of silicon, sulfur, and germanium nitrides [19, 21– 25]. The gate oxide reliability is ascribed to the fact that interfacial defects behave as charge traps [2]. The oxides of group IIIB – such as Y_2O_3 – previously used for stabilizing amorphous germanium oxide and resulted in the electrical reliability enhancement of the gate oxide [26, 27]. Following, the first-principle mechanism of how metal doping within the oxide network will stabilize the oxide will be discussed.

Empirically, the enhancement of germanium oxide stability after yttrium doping is associated with having a more robust oxide network, and this finding has made yttrium a beneficial metal for GeO₂ stability improvement [26]. From the Density Functional Theory (DFT) point of view [2], there are two types of defects in a GeO₂ network: O vacancy and Valance Alteration Pairs (VAP). In the case of SiO₂, the vacancy energy of formation is much greater than that of GeO₂ [2], and that is why GeO_2 is a more unstable oxide compared to SiO_2 . As is shown in Figure 1.2a, in a crystal of GeO₂, the generation of O vacancy leaves two Ge dangling bonds, resulting in the reconstruction of Ge-Ge bonds. This happens likewise in the case of SiO₂ [2, 28]. Li's DFT study [2] also suggests that VAP states are the result of breaking the earlier-mentioned Ge-Ge bond in Figure 1.2a. By breaking the Ge–Ge bond, two threefold coordinated Ge atoms will be resulted. Flipping one of the three-folded germaniums from the O vacancy site towards an oxygen atom at the opposite side, results a new Ge–O bond with a positively charged three-folded O and a negatively charged three-folded Ge atom (at the original site), based on the octet rule. This leads to having a pair of electrons in the band gap of GeO₂, which is known as VAP states. As is shown in Figure 1.3 these states are energetically close to the band edge of Ge. The substitution of two Y atoms with the two Ge atoms involved in VAP states will encourage those two electrons fall from the GeO₂ band gap to the valence band because Ys substitution generates two

holes in the valence band. Therefore, the oxide will be stabilized.



Figure 1.2: O vacancy and Valance Alteration Pairs (VAP) in a crystalline GeO₂; Ge: green atoms, O: red atoms, Ge1, Ge2, and Ge3: altered Ge atoms in the oxide network, and O involved at VAP: orange atom. The figure is reproduced from [2], with the permission of AIP Publishing.

As shown in Figure 1.3, O vacancy defects are not energetically very close to Ge band edges, meaning that they are less prone to trap charges, while VAP states (both empty and filled gap states) are close to Ge band edges and are more effective charge traps. Overall, the passivation of O deficiency releases lower energy than that of VAP [2]. Likewise, there might be a similar mechanism for other metal oxides – such as Al₂O₃, HfO₂, Sc₂O₃, Y₂O₃, and La₂O₃ – which can be doped into GeO₂ structure to improve thermal stability [27]. These materials possess a network-strengthening effect, directly related to the number of Metal–O bonds.

Being water-soluble, GeO_2 incurs problems in the device fabrication process [6, 9, 23, 25, 29–31]. Upon exposing to air, the device absorbs water which causes the degradation of electrical properties [32]. This will make GeO_2 unsuitable as a gate oxide material. Therefore, one needs to come up with a solution to not only reduce the water solubility but also mitigate the defects of GeO_2/Ge interface. The doping of the above-mentioned metals will increase the length of etching time in Metal–GeO₂/Ge stack. As a result, water resistivity of the oxide will be enhanced [27, 32]. This lies in the fact water resistivity improves with an increased



Figure 1.3: The band alignment of Ge and GeO₂ and defect levels of (a) O vacancy and (b) VAP, summarizing the passivation mechanism of Y in the band alignment. The figure is reproduced from [2], with the permission of AIP Publishing. [2].

number of M-O bonds [27].

Also, this metal doping will lead to an enhanced thermal stability due to reducing the Gibbs energy of formation of oxide. GeO_2 has higher Gibbs energy of formation compared to SiO₂. Thermal stability of GeO_2 is enhanced after doping an oxide such as Y_2O_3 which has a lower Gibbs energy of formation [32].

Equation 1.1 shows the reduction reaction of GeO₂ to GeO at the Ge interface. From the equation, due to the high reactivity of GeO₂/Ge interface, at temperatures higher than 400 °C, GeO₂ will be chemically reduced and volatile GeO will be formed [6, 29, 33, 34], while such a case for SiO₂ happens at higher than 1100 °C [8]. The desorption of GeO at/near the dielectric/substrate interface gives rise to the number of charge traps. Even when there is no intentionally grown GeO₂ interlayer e.g., in the case of high- κ /Ge, the presence of GeO is inevitable due to interfacial Ge–O bonds [6] as a result of the intermixing of Ge and O atoms between high- κ and Ge substrate.

$$\text{GeO}_2 + \text{Ge} \longrightarrow 2 \text{GeO}.$$
 (1.1)

By replacing the anion or cation atom in GeO_2 by a metal or nitrogen, a more stabilized oxide will be obtained as a dielectric layer [6], and the Equation 1.1 will be restricted due to the following equation:

$$\text{GeO}_2 \longrightarrow \text{GeMO} \text{ or GeON}$$
 (1.2)

where M represents a metallic atom and N is nitrogen.

The presence of GeO at the interface deteriorates electrical properties, e.g., C - V characteristics. Equation 1.3 represents the most important reaction in the fabrication process of a Ge-MOSFET. In interaction with a Ge surface, at 400 °C and above, GeO₂ is reduced to GeO(s) or GeO(g) [19, 34–36]. GeO(g) molecules can leave the interface through the GeO₂ layer [8]. Kita *et al* [19] have observed that GeO desorption results in a huge hysteresis in C - V characteristics of an Au/GeO₂/Ge gate stack and considerable change of flatband voltage to the negative direction. A large amount of interfacial defect states (charge traps) is generated due to GeO desorption, which is in charge of degrading electrical properties.

$$\text{GeO}_2 + \text{Ge} \longrightarrow 2 \text{GeO}(\text{s}) \text{ or } 2 \text{GeO}(\text{g}) \text{ at } 400 \,^\circ\text{C}$$
 (1.3)

It is essential to passivate defect states at the oxide/substrate interface. Ge dangling bonds are a type of defects that results in high interface state density. Dangling bonds, in chemistry, are unsatisfied valance on an immobile atom. They are so reactive and can play the role of negatively charged traps [17]. Determining the number of dangling bonds is crucial and mitigating them at the interface is of paramount importance because they can deteriorate electrical properties. Over time, high interface state density will result in higher gate leakage current and degrades the threshold voltage. With this, suppressing the number of Ge dangling bonds is pivotal in Ge-MOSFETs. It is worth noting that the conventional hydrogen passivation which is effective in SiO₂/Si gate stacks, is not in effect for GeO₂/Ge ones. In this dissertation, I propose some fabrication-level solutions to mitigate the

high density of interfacial dangling bonds at GeO₂/Ge interface.

1.5 The Necessity of High- κ Materials

Upon studying the electrical degradation of a MOSFET due to interfacial defects (within dielectric/substrate region), one needs to consider both bulk and interface characteristics. As mentioned earlier, the existence of germanium native oxide between the high- κ and substrate layers is unavoidable. Meanwhile, to reach a high-performance MOSFET, high- κ materials are required. In order to achieve smaller transistors to densify ICs, a shallower gate oxide with a high dielectric constant is required. However, thin native oxides result in higher gate leakage current, and, this is when high- κ materials yield benefits. In fact, based on Equation 1.4, high- κ materials enable smaller MOSFETs with a thinner gate dielectric thickness, but higher gate capacitance [8].

$$C = \frac{A\varepsilon_0\varepsilon_r}{d} \tag{1.4}$$

where *A* is the capacitor area, ε_0 and ε_r are the vacuum and relative permittivity respectively, and *d* is the thickness of the gate dielectric. In order to increase the gate capacitance, while using thinner oxide to meet the design requirements, a dielectric material with a high κ -value is required. Although HfO₂ on the Ge substrate is not a suitable oxide due to resulting a large leakage current, it has shown proper characteristics on the Si substrate [6, 36]. Yet, there are other alternatives exhibiting good electrical properties on Ge substrates such as GeON, GeAION, GePO, GeYO, GeZrO, GeZrSiO [6], and some others in Ref. [27].

Through this research, I have innovatively put forward a new method to enhance both the dielectric constant and interface quality.

1.6 Work Contributions and Outline

Thus far, the existing problems in Ge-MOSFETs have been reviewed in this Chapter. This dissertation is organized as follows. In Chapter 2, the applied method in this research is explained. The focus is on the Molecular Dynamics (MD) foundations and the specifications and details of the simulations carried out in this research. Next, the tools and software utilized throughout this research are introduced. Then, the specifications of different systems developed to address the existing issues of Ge-based MOSFETs and improving the gate stack is presented.

In Chapter 3, the simulation results of the systems described in Chapter 2 are presented. First, the nature of germanium native oxide, when it comes to reacting with the Ge substrate, is discussed. The impact of changing the thickness of the dielectric layer on the number of interfacial defects at the dielectric/substrate interface is analyzed. Next, the types of germanium interfacial dangling bonds responsible for the degradation of electrical properties, are investigated. A dipole effect near the interface of the dielectric/substrate is presented. The doping of Ge with Al is studied and characterized.

In Chapter 4, conclusions are drawn and future work is presented.

Chapter 2

Method and Tools

Molecular Dynamics (MD) is the adopted computational approach in this study because it offers high computational speed with less complexity compared to other simulation methods such as Density Functional Theory (DFT). Also, the combination of MD and Reactive Force Field (ReaxFF) compensates for the inherent lack of accuracy of classical Molecular Dynamics (MD).

2.1 Simulation Approaches for Computational Chemistry

As Figure 2.1 depicts, experiments, theories, and numerical simulations (computation in general) are tightly bound as the parts of a comprehensive scientific work. Simulations are usually conducted when the real system is not accessible, the realworld experiment is impractical, impossible, or costly (time- and money-wise). It is an assessing tool for engineers to test theoretical models and predict/verify experiments. The scientific work initializes with theories, and then, it comes to experiments. Simulations help bridge the gap between the theory and experiment. Although experiments can be more accurate, simulations are faster and more financially efficient. Since each process needs a number of iterations to achieve optimal parameters, with the associated costs added, by employing simulations, those costs would be significantly reduced.

Particularly, the computational chemistry models systems at atomic scale and



Figure 2.1: Different parts of scientific work.

is generally divided into three categories [37]:

- *Ab-initio* methods that are rigorously based on Quantum Mechanics: due to the limitation of computing power, this is restricted to small systems with the approximate size of 10² atoms.
- Smei-Empirical methods that are approximately based on Quantum Mechanics: suitable for systems with approximate size of 10⁴ atoms.
- Molecular Dynamics methods that are based on Classical Mechanics and able to model systems with extensive size of 10¹² atoms.

Herein, I employed Molecular Dynamics simulations through which the behaviour of the system is studied by numerical integration of the Newton's second law ($\vec{F} = m \times \vec{a}$) over time.

2.2 Molecular Dynamics Foundations

Molecular Dynamics (MD) is a numerical method for studying the systems with many particles at microscopic scales such as molecules and clusters, or macroscopic scales such as gases, liquid, and solids. Alder and Wainwright [38] initially established MD. Thanks to the advancement of computing power, different software packages have been introduced to implement cutting-edge scientific methods in the area of Molecular Dynamics. In this area, Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [39] is a General Public License software that has been developed by Sandia National Lab, USA. In this dissertation, LAMMPS was employed as the major simulation tool along with Reactive Force Field (ReaxFF) initially developed by Adri van Duin [1, 40].

There are two different classes of Molecular Dynamics simulations: classical and *ab-initio* (first-principle) MD. In classical MD, interactions are modelled and approximated using empirical potentials which are established in accordance with experiments. The classical MD is fast and enables one to simulate large-scale systems based on the laws of classical physics. However. in *ab-initio* MD, one deals with quantum calculations of the electronic structure. Although enjoying higher accuracy, *ab-initio* MD requires considerably more computational power, which restricts the simulation time and the number of involved particles. This research adopted the classical MD approach that enables a longer simulation time and modelling a larger system of atoms.

In MD simulations, each particle is assumed to have coordinates based on which potential functions are used to compute the interactions between them. Assigning appropriate potential functions, which are called "force fields" in the MD community, to each particle is essential. There are different force fields employed based on the application [1, 41–43]. In comparison with quantum-mechanical and semi-empirical methods, the Reactive Force Field (ReaxFF) has shown a faster performance, while maintaining a good accuracy at the same time [1]. It enables the MD simulation of systems with thousands of atoms.

Engaging the relationships between bond order and distance, and bond order and energy empowers ReaxFF to allow for ongoing bond dissociation and formation during the simulation period. In chemical reactions, bonds are broken and reformed continuously until reaching equilibrium. However, in non-reactive force fields, angle energy follows a quadratic behaviour [44], and they are precise for the cases in which the molecular bond lengths and angles are in the near-equilibrium state, making these force fields unsuitable for simulating chemical reactions. However, in ReaxFF, which bridges the gap between non-reactive force fields and DFT, the system energies are accurately predicted even in non-equilibrium states. Stressing, straining, or changing the system temperature can shift the equilibrium, and

Number of Atoms	ReaxFF time (s)	Semi-empirical (PM3) time (s)	DFT time (s)
100	0.4	10.0	12500
200	0.8	100	100000
300	$0.9 \sim 1$	400	125000

 Table 2.1: Comparison between computational costs of DFT, PM3, and ReaxFF [1].

that is why ReaxFF brings advantages for more accurate chemical reaction simulations.

Regarding the computational resources required for the study, although being computationally more accurate, quantum-mechanical methods – such as DFT – require a large amount of computational resources for a system with a limited number of atoms (few hundreds of atoms). In addition, they are limited to shorter simulations time span. ReaxFF can bridge the gap between quantum chemistry and the bulk methods, which involve more atoms and can be run longer at lower computation cost [44]. Table 2.1 compares the computational expense between DFT, semi-empirical (e.g., Parameterized Model number 3 (PM3)), and ReaxFF.

In this research, I selected MD because the rate of processes must be known (e.g., cooling rate of the melted oxide). Also, for the scale of my system, based on the previous studies [45, 46]

2.2.1 Involved Steps In An MD Simulation

The procedure of a Molecular Dynamics simulation includes several steps. Figure 2.2 summarizes the major steps involved.

- Defining the system: defining what the system is to undergo, which affects the involved atoms (e.g., kinetic energy) within the system.
- The properties intended for calculations: clarifying the properties I are interested in studying and modelling.
- Determining the interactions and proper force field: the force field is the

heart of an MD simulation and determines how the involved atoms interact. Therefore, upon understanding the nature of the system, choosing an appropriate force field, which generates a precise molecular structure compared to experiments, is crucial.

- Initial data: the spatial structures of particles, temperature, pressure, volume, and density are all important data needed to be specified for each MD simulation.
- Molecular simulation methods: Monte Carlo (MC) and Molecular Dynamics (MD) are among molecular simulation techniques, the choice of which depends on the phenomenon being studied. The advantage of MD over MC is providing one with the system's dynamic properties such as transport coefficients and rheological properties.
- Simulation box: in each MD simulation, particles are placed in a box within which one implements the operating conditions of the simulation, e.g., temperature, pressure, force, to name but a few. The box is the simulation space inside which the atoms and molecules are accommodated.
- Execution: there are many ways to execute an MD simulation, either coding everything using a programming language or using MD software, such as LAMMPS, GROningen MAchine for Chemical Simulations (GROMACS), Nanoscale Molecular Dynamics (NAMD), and Materials Studio, the use of which yet depends on the application and the phenomenon being studied.
- The validation of the results: this last step comes into effect for analyzing and post-processing the simulations results. Using the experimental data and literature, one can validate if the simulation is capable of predicting other systems that have not been studied.

2.2.2 Velocity-Verlet Algorithm

Across an MD simulation, based on the frequency of outputs, atomic trajectories are rendered and integrated. The integration method of use on Newtonian formulation must possess some features to ascertain a reliable simulation, similar to



Figure 2.2: General simulation flow diagram of an MD simulation.

real-world systems. Equations of motion are second-order ordinary differential equations (ODE), and one can use any integration method to integrate over them. There are different integration algorithms to be used through MD simulations such as velocity-Verlet, Brownian dynamics, rigid body integration, to name but a few.

While simple, velocity-Verlet [47] algorithm is one of the fastest, most reliable, accurate, and popular methods. Equation 2.1 and Equation 2.2 show the algorithm, and Equation 2.2 is obtained by deriving $\vec{a}(t + \Delta t)$ from $\vec{r}(t + \Delta t)$ as follows:

$$\vec{r}(t+\Delta t) = \vec{r}(t) + \vec{v}(t)\Delta t + \frac{1}{2}\vec{a}(t)\Delta t^2$$
(2.1)

$$\vec{v}(t + \Delta t) = \vec{v}(t) + \frac{1}{2}(\vec{a}(t) + \vec{a}(t + \Delta t))\Delta t$$
 (2.2)

where $\vec{r}(t)$, $\vec{v}(t)$, and $\vec{a}(t)$ are the spatial positions, velocity and acceleration of particles, respectively. $\vec{a}(t)$ is obtained from Equation 2.3, where *U* is the potential energy constructed based on the employed force field, and Equation 2.4.

$$\vec{F} = -\nabla \vec{U} = -\frac{\partial U(\vec{r})}{\partial \vec{r}}$$
(2.3)

$$\vec{F} = m \times \vec{a} = m \frac{\partial^2 \vec{r}}{\partial t^2}$$
(2.4)

The velocity-Verlet algorithm is only applicable when there is no restriction applied to the system. In restricted cases, such as when one utilizes thermostats and barostats to control the pressure and temperature of the system, the velocity-Verlet algorithm will change. For instance, in my simulations Nosé-Hoover [48, 49] thermostats are employed to control the temperature and pressure. By creating a feedback loop, such thermostats change the velocity-Verlet algorithm to control the kinetic energy.

2.2.3 Thermostats and Ensembles

In order to control the operating conditions of the system, there are several proposed algorithms. All these algorithms (barostats and thermostats) can be utilized in MD simulations for pressure and temperature control. Thermostats and barostats function based on the associated time steps in order to couple to the dynamics of the particles. The time step defines the sensitivity of the pressure and temperature oscillations. The time steps need to be slow enough to control the oscillations of temperature and pressure, but if too slow, the equilibrium at the desired temperature and pressure will not be achieved in a reasonable simulation period or the simulations will not converge.

The thermostat and barostat of choice in this research is Nosé-Hoover [48, 49] with Number-Pressure-Temperature (NPT) and Number-Volume-Temperature (NVT) ensembles.

In a thermodynamic system, the state of the system is represented by several parameters such as temperature (T), pressure (P), and number of particles (N). At any given time, a complete set of particles position and momenta defines the microscopic state (microstate) of a macroscopic system, e.g., kinetic energy, particles velocity. A macroscopic system is a system with many particles, e.g., electrons, photons, atoms, and molecules. While the macrostate (e.g., pressure, temperature, and volume) of a system can remain constant, the microstates can change constantly every moment. An *ensemble* is the collection of microstates of all possible systems which have an identical macroscopic state [50]. In an MD simulation, there are different ensembles:

- Microcanonical ensemble (Number-Volume-Energy (NVE)): This ensemble characterizes the thermodynamic state by a constant number of atoms, constant volume, and constant energy. Therefore, this represents a system which is isolated energetically.
- Canonical ensemble (Number-Volume-Temperature (NVT)): This ensemble characterizes the thermodynamic state by a constant number of atoms, constant volume, and constant temperature.
- Isothermal-isobaric ensemble (Number-Pressure-Temperature (NPT)): This ensemble characterizes the thermodynamic state by a constant number of atoms, constant pressure, and constant temperature.

2.3 Simulation Tools and Specifications

2.3.1 Tools and Softwares

As mentioned earlier, the classical Molecular Dynamics simulations in this research were carried out using LAMMPS software package [39, 51], the release of June 28, 2014. The employed ReaxFF in this work was developed by Zheng *et al* [45]. This force field has been developed for a system which has Al/C/H/O/Ge atoms as its constituents. Finally, the simulation results were visualized using Ovito software [52].

2.3.2 Simulations Specifications

GeO₂/Ge Interface

A slab of Ge(100) with the thickness of 45.26 Å was cleaved. For the dielectric layers, an alpha-quartz GeO₂(100) was prepared, cleaved and placed on both Ge interfaces with an initial gap of 2 Å. The dimensions of the simulation box, in which the oxide/substrate structure was fitted, are $22.63 \times 22.63 \times 87.41$ Å³. Accordingly, the density of alpha-GeO₂ placed on the Ge substrate within the simulation box is $3.58 \ g/cm^3$. Figure 2.3 depicts the prepared structure before the execution of simulations.



Figure 2.3: The simulation box which contains a Ge substrate layer sandwiched between GeO_2 gate oxide layers with initial 2 Å gaps. Ge = green atoms, O = red atoms.

A periodic boundary condition in all three Cartesian directions was chosen for all the simulations in this study. Also, the earlier-mentioned Nosé-Hoover thermostat was employed for the temperature regulation. Next, the system was minimized energetically, and, subsequently the system's energy was equilibrated using a micro-canonical ensemble (NVE), at 300 K. Afterwards, using a constant NVT ensemble, the substrate and oxide got to react with each other by heating the system up to 500 K. To ensure the chemical reaction between the oxide/substrate, the system was retained at 500 K for 100 ps, then linearly cooled down to 300 K. Next, the whole structure was equilibrated at 1 atm and 300 K by a constant NPT ensemble. Last, the system was thermally annealed to relieve the internal residual stress introduced to the system during the process. This thermal annealing process is a part of semiconductor fabrication process. In this regard, the system temperature was elevated to 900 K, which is the half of the melting point of GeO_2 , and cooled back down to 300 K. The time step of choice at this stage of simulations was 0.2 fs. Figure 2.4 shows the entire simulation paths taken in this part of the research.



Figure 2.4: The entire simulation paths for preparing the interface of GeO_2/Ge .

The time breakdown of the simulation steps is as follows:

- NVE: 10 ps
- NVT: 1 ns
- NPT: 50 ps
- Annealing process: 500 ps

As shown in Figure 2.4, I repeated the simulations for different cooling rates

the effect of them on the formation of interfacial defects. Specifically, cooling rates of 2×10^{12} , 2×10^{13} , and 2×10^{14} were tested.

Bulk Oxide Preparation

As discussed earlier in Section 1.3, shallow thicknesses of gate oxide is desirable. I investigated the effect of oxide thickness on the interface quality. In order to grasp the relationship between the oxide thickness and the number of GeO_2/Ge interfacial dangling bonds through my MD model, first, one needs to generate the amorphous gate oxide. Therefore, starting from an oxide crystal, to prepare the amorphous oxide and disorder the crystal structure, the oxide needs to undergo a high-temperature annealing process. As a result of the annealing process, the system's kinetic energy increases and atoms start vibrating within the crystal, and eventually, leave the crystal network. Subsequently, through a slow cooling process, the atoms will reach equilibrium and be repositioned inside the crystal network. It is important to allow atoms to reach the equilibrium by a slow cooling rate; otherwise, they may not reach to a minimum energy configuration.

The system specifications of previous studies [45, 46, 53] provided me with insights to choose my simulations parameters, e.g., the box size, cooling rate, and the simulation period. Accordingly, as shown in Figure 2.5, another crystal of alpha-quartz GeO₂(100) was cleaved and placed in a simulation box with the dimensions of $22.63 \times 22.63 \times 30 \text{ Å}^3$. The cleaved oxide possessed the oxide density of 3.77 g/cm^3 , and the simulation box contained 990 atoms in total. Generally, MD simulations time duration is short (pico to microseconds). Accordingly, I chose a somewhat higher heating temperature of 1500 K than the α -GeO₂ melting point (1389 K [54]) to ensure the whole crystal is melted and randomized entirely throughout the designed simulations. In particular, to disarrange and deform the crystal structure, the simulation cell was retained at that temperature for 30 ps, and, subsequently cooled down to 300 K in 600 ps with a cooling rate of 1.8×10^{12} K/s. Then, the system's pressure and the temperature were equilibrated at 1 atm and 300 K, respectively, for 50 ps using an NPT ensemble.

Then, oxide slices with different thicknesses of 3, 4, 5, and 6 Å were cleaved from the prepared amorphous GeO₂. A Ge substrate with 22.63 Å length in all


Figure 2.5: The snapshot of the alpha-GeO₂ bulk oxide before heating and cooling processes. Ge = green atoms, O = red atoms.

three directions was sandwiched between those cleaved slices. Then, the system was heated up to 500 K and linearly cooled to back 300 K, accompanied by equilibration at 300 K and 1 atm. Likewise, the thermal annealing was performed to release the imposed stress to the system.

2.3.3 Dielectric Constant Calculation

The dielectric constant (κ) or relative permittivity (ε_r) is a physical property of materials showing how much an externally-applied electric field will be opposed by the molecules. This property is important to be calculated for a dielectric medium. It will be shown that the designed reactive MD simulation is capable of computing dielectric constant with a good precision, but there is a constraint in calculating the dielectric constant of denser forms of GeO₂. Specifically, for a dense oxide – such as tetragonal GeO₂ – the employed force field is not capable of handling the simulation because there is not enough space inside the simulation box for the atoms so that the dipole moments are calculated.

There are different crystal phases for GeO2: hexagonal (alpha-quartz structure),

tetragonal (rutile structure), and amorphous. These three different crystals of GeO_2 were aimed for the dielectric constant calculations. The density of the oxide is an influencing factor on the dielectric constant with respect to Kamata [6] and our simulations. As mentioned earlier, one of the challenges of using the employed ReaxFF in this work is inability to simulate tetragonal GeO₂, a dense form of GeO₂ with a density of 6.24 g/cm³.

Being known that the dipole fluctuation of the system is related to the dielectric constant [55], I analyzed the system's dipole fluctuations over time. Previously, this method was employed using MD simulations for water-based systems [56, 57]. For the dielectric constant calculations, to ensure the convergence of dipole moments, MD simulations were carried out for 10 ns. For tetragonal GeO₂ an NVT ensemble, and, for the hexagonal GeO₂ an NPT was employed. The temperature in effect is 300 K. Given the fact that I want the system to reach the equilibrium within a large simulation time span, a large time step of 1 fs was chosen at this stage.

To prepare the above-mentioned GeO₂ structures the following procedures were followed. A unit cell of quartz-like germanium dioxide developed by Smith [58] was utilized to prepare a simulation box of tetragonal GeO₂ with the dimensions of $24.92 \times 21.58 \times 22.59 \text{ Å}^3$. Also, a unit cell of a rutile-like germanium dioxide [59] was generated with the dimensions of $21.98 \times 20.01 \times 21.98 \text{ Å}^3$. Last, an amorphous GeO₂, which was prepared earlier in Section 2.3.2, was reemployed for dielectric constant calculations.

In this work, the the dipole moments of the systems were collected every 100 fs. As suggested in Ref. [57], the collected dipole moments are used for determining the low-frequency permittivity using the following equation:

$$\varepsilon = 1 + \frac{\langle M^2 \rangle - \langle M \rangle^2}{3\varepsilon_0 V k_B T}$$
(2.5)

where ε_0 is the permittivity of vacuum, *V* is the MD simulation cell volume, k_B is the Boltzmann constant, *T* is the temperature, *M* is the total dipole moment, $\langle M^2 \rangle$ is the average of M^2 , and $\langle M \rangle^2$ is the square of average *M*.

2.3.4 Aluminum Doping of GeO₂

As mentioned earlier, one way of improving oxide quality is incorporating several metals into the oxide network. Doing so, the water solubility of the oxide reduces and it becomes more stable. Also, there are some metals such as yttrium, discussed earlier in the introduction, inclusion of which improves the oxide by forming a stronger oxide network. Basically, doping yttrium exists in the form of Y^{3+} cation which bonds to the nearest oxygen atoms and makes the oxide structure more robust [32]. Thus, in this research, I studied the effect of doping Al into the GeO₂ on shifting the number of dangling bonds at the interface. Following, the materials development will be discussed.

As a result of doping Al into GeO_2 crystal network, there are two possible outcomes which I hypothesized and investigated. Therefore, this part of research divides into the two following sections:

- What is the impact of doping Al on interfacial defects at the oxide/substrate interface?
- What is the impact of doping Al on the dielectric constant of oxide?

To answer these questions, several structures were formed which are explained in below. In addition, appropriate simulation specifications were attributed to both systems.

The Effect of Aluminum Doping on Interface Quality

Different dilute Al atomic concentrations were introduced to GeO_2 oxide. Since the subject of investigation in this part of the research is the effect of Al doping on the interfacial defects, Al atoms were introduced near the interface vicinity. Oxygen tends to oxidize aluminum with the O-to-Al ratio of 1.5 to form Al_2O_3 . Accordingly, this ratio was retained within all of the samples after doping Al.

A phase segregation happens inside the oxide layer if a large amount of metallic atoms is introduced to this layer. So, the GeO_2 was doped with dilute Al concentrations due to previous findings with respect to Y. In the case of Y-doped GeO_2 , Lu *et al* [32] previously reported that if the atomic concentration of yttrium increases from 10% to 30%, it will bring about higher gate leakage current due to

the formation of new conductive paths. These conductive paths are formed due to the phase segregation of GeO_2 and Y_2O_3 as a result of excessive Y-doping. This is also the case for other metallic atoms [32]. As a result, in order to prevent the phase segregation within the oxide layer, in this research, dilute concentrations of Al (below 10 at. %) were selected to dope the GeO₂ with.

Aluminum atoms were doped inside the GeO_2/Ge interface prepared in Section 2.3.2. Since the substrate was sandwiched between two oxide layers, there are basically two surfaces available. Thus, the samples contain 0, 10, 15, 20, and 25 Al atoms per interface. Figure 2.6 displays zoomed-in structure of two samples with 10 (Figure 2.6a) and 25 (Figure 2.6b) Al atoms doped near the interface of GeO_2/Ge before starting the simulations. Also, the space between two layers is the initial 2 Å gap.



Figure 2.6: Zoomed-in snapshots of aluminum-doped GeO_2 gate oxide and Ge substrate before beginning the simulations with initial 2 Å gap. Ge = Green atoms, O = red atoms, Al = yellow atoms.

Next, all samples, ranging from zero to 25 Al atoms, underwent the same operating conditions. Therefore, orthogonal simulation boxes were prepared with all samples fitted in. The dimensions of the boxes were the same as before, $22.63 \times 22.63 \times 87.41 \text{ Å}^3$. First, the prepared samples were minimized energetically, and, then using an NVE ensemble, their energy was equilibrated at 300 K. Afterwards, they all were heated up to 500 K, followed by a cooling process down to 300 K within 175 ps. Then, using an NPT ensemble the pressure and temperature of the systems were equilibrated at 1 atm and 300 K, respectively.

Again, for the purpose of as a part of semiconductor fabrication process, an annealing process is performed on the sample to release the stresses imposed on the system. relief, all simulation boxes received thermal annealing. The boxes were heated up to 900 K, and then cooled down to room temperature, 300 K.

Aluminum Doping Effect on The Dielectric Constant

To answer the second question posed, I investigated the effect of Al doping on the dielectric constants of different Al-doped GeO₂ samples. In particular, using the formerly-prepared bulk oxide, depicted in Figure 2.5, I generated five different orthogonal simulation boxes containing different atomic concentrations of Al. Similar to the previous part, dilute concentrations of aluminum – 10, 15, 20, and 25 Al atoms – were doped into the hexagonal GeO₂ crystal network. In order to have all the samples undergone the same heating and cooling process within the same simulation time span, I generated one oxide sample without any Al doped.

Within all the prepared samples, I considered the fact that aluminum tends to intermix with oxygen with the O-to-Al ratio of 1.5 to form Al₂O₃. In addition, the oxide density of all samples retained close to each other, $3.71 \pm 0.04 \ g/cm^3$.

Next, similar procedures to what was described in Section 2.3.3 was followed to calculate the dielectric constant of the samples.

2.3.5 Structural Properties

Radial Districution Function (RDF)

If MD trajectories are properly generated, they will result in various structural properties. Radial Districution Function (RDF) or partial pair correlation function $(g_{\alpha\beta}(r))$ is a structural property that, in a system of particles, as depicted in



Figure 2.7: Calculation of g(r).

Figure 2.7, determines the probability of finding a particle at a specific distance (r) from a reference particle. RDF plots exhibit several sharp peaks within a solid structure. The separation and height of each of those sharp peaks correspond to the lattice structure characteristics. The Radial Districution Function can be obtained both through simulations and experiments, e.g., X-Ray scattering. Therefore, the RDF obtained from an MD simulation is comparable with experimental results. For a system of two particles, the probability of having β species in the neighbourhood of α species (inside a spherical shell between *r* and $r + \Delta r$) is defined as follows [60]:

$$g_{\alpha\beta}(r) = \frac{\langle n_{\alpha\beta}(r + \Delta r) \rangle}{4\pi r^2 \Delta r \rho_{\beta}}$$
(2.6)

where $\rho_{\beta} = N_{\beta}/V$ is the number density of β species, in which N_{β} is the total number of β atoms. To calculate $n_{\alpha\beta}$, the number of β atoms should be counted in a shell with a small-enough thickness of Δr at the distance of r from the reference species, α .

Average Coordination Number

One can determine the number of neighbours around an atom by calculating the integral of the first minimum in RDF plot. From Equation 2.6, the running coordination number can be calculated as follows:

$$n_{\alpha\beta}(R) = 4\pi\rho_{\beta}\int_{0}^{R}g_{\alpha\beta}(r)r^{2}dr \qquad (2.7)$$

where $n_{\alpha\beta}(R)$ is the running coordination number at the cut-off radius of R. By plugging the first minimum of RDF plot at *R* in Equation 2.7, the average coordination number of atoms β in the shell of atoms α will be obtained. In other words, the surface of the first peak will provide the average coordination number of such atoms.

Chapter 3

Results and Analysis

3.1 GeO₂/Ge Interface Quality Enhancement

After the generation of the oxide/substrate interface, GeO_2 showed the tendency towards being in amorphous phase near the substrate. In other words, the closer to the interface, the more amorphous oxide tends to be. As Figure 3.1 exhibits, once the distance increases from the interface, GeO_2 structure changes to its previous state – alpha crystal. There are different crystal phases for GeO_2 : hexagonal (alpha-quartz structure), tetragonal (rutile structure), and amorphous. Among these structures, being water soluble, hexagonal and amorphous structures will result in the adsorption of the air water content [6, 31]. My observation confirms that the existence of GeO_2 amorphous nature is inevitable near the substrate interface, so the previously mentioned problem regarding water solubility [6, 9, 23, 25, 29–31] is still in effect in this work.

Figure 2.3, 3.1, and 3.2 depict three stages of the system. First, the system depicted in Figure 2.3 is prior to energy minimization and equilibration. Upon starting the energy minimization, the oxide layers start relaxing, and they come closer to the substrate interact with the interface. Figure 3.1 shows the system after energy minimization, when the layers are relaxed energetically. The Figure 3.1 illustrates that the oxide layers at the interface changed to amorphous oxides, while the oxides at farther distances from the interface are still crystalline. After the energy minimization, the system was thermally annealed at 500 K, followed by a



Figure 3.1: Crystal deformation of α -GeO₂ after energy minimization for 10 ps at 300 K. Ge = green atoms, O = red atoms.



Figure 3.2: Ge slab sandwiched by two layers of GeO_x at the end of NPT steps, 1.1520 ns.

cooling process as described earlier in Section 2.3.2. Figure 3.2 illustrates the system structure at the end of simulation period, 1.1520 ns. Based on the Figure 3.2, both oxide layers are fully randomized, and they lost their grain boundaries, even at farther distances from the substrate. The grain boundaries result in slower carrier transport, which yields smaller current, slower switching speed, which causes more heat generation, and higher gate leakage current, which leads to higher power usage. Yet, as shown in Figure 3.2, few small rings of the previous ordered crystal structure have been remained at farther distances inside the oxide.

Figure 3.3 depicts the oxide transition from suboxide to oxide. In other words, I investigated how the ratio of O to Ge atoms changes when moving from the oxide/substrate interface towards the farther distances within the oxide. As a result of cleaving and accommodating the crystal oxide into the simulation box, the original O to Ge ratio for the crystal of alpha-GeO₂ was not two. The results reveal that GeO₂ is more of a suboxide at the interface. This is aligned with previous studies which have stated GeO desorbs from the interface of GeO_2/Ge during the thermal annealing [6, 19].



Figure 3.3: The ratio of oxygen to germanium atoms in GeO_x vs. the distance from the surface.

In quantum MD, simulations run in the time span of picoseconds, but as we demonstrate in this work, by utilizing ReaxFF it is possible to simulate the system for periods up to nano and microseconds at lower computational costs. The longer the simulations run, the more accurate the results will be.

To calculate the number of Ge dangling bonds at the GeO_2/Ge interface, which are the type of defects investigated in this part of the dissertation, some structural properties of GeO_2/Ge such as Radial Districution Function (RDF), the bond length of involved atoms, and the average coordination number need to be analyzed and calculated. The structural properties of the system were analyzed and compared with other experiments and simulation-based studies.

As shown in Figure 3.4, with the employed ReaxFF in this work, the Ge–O bond length was found to be 1.8 Å, Ge–Ge to be 2.4 Å, and that of O–O to be 2.8 Å. Also, the cut-off radius of 2.6 Å is obtained from Figure 3.4, which is the minimum after the first peak of g(r) on the RDF plot. Accordingly, I determined the Mean Coordination Number (MCN) of Ge and O atoms. Table 3.1 summarizes the bond lengths and cut-off radii extracted from Figure 3.4. The results of this analysis was used to calculate the number of interfacial dangling bonds at the GeO₂/Ge interface.



Figure 3.4: Radial Distribution Function of the system at end of the simulation.

After obtaining the bond lengths from the RDF plot, I calculated the MCN of

Atom Pair	Bond Length [Å]	cut-off Radius [Å]
Ge-O	1.8	2.6
Ge-Ge	2.4	2.8
0-0	2.8	4.2

Table 3.1: The inter-atomic lengths of the involved atoms in the simulation, resulted from partial pair correlation function.

Ge and O atoms. Figure 3.5 shows the MCN analysis for the involved atoms inside the system. As a result, the MCN of Ge atoms in the system was 4.21 and that of O atoms was 2.68.



Figure 3.5: The Mean Coordination Number (MCN) analysis of germanium and oxygen atoms within the oxide layers vs. radius at the end of the simulation.

As mentioned earlier, an annealing process needs to be performed to release the stress imposed to the system during the heating and colling process. Accordingly, within the time span of 500 ps, the system was heated up to 900 K using an NVT ensemble, then cooled down to 300 K and equilibrated at 1 atm. A reduced number of Ge dangling bonds was evident after this annealing process, resulting in fewer interfacial defects. On average, my simulations demonstrated a 33% decline in the number of dangling bonds after this thermal annealing process throughout the last 20 time steps. Consequently, in addition to releasing the imposed stress to the system during the fabrication process, annealing results in a more uniform interface with fewer number of defects.

The oxidation temperature of germanium is an important factor in the fabrication process of MOSFETs. In [17], the authors suggested a closed-form expression that relates the GeO₂ viscoelastic properties to its oxidation temperature. In detail, they showed that there is an inverse relationship between the density of interfacial defects and the oxidation temperature at which the Ge substrate is oxidized by O atoms. In addition, Nakakita [61] suggested that the GeO₂/Ge interface roughness and the density of Coulomb scattering centres are reduced at higher oxidation temperatures. In this study, this oxidation temperature which is one of the known factors impacting the generation of interfacial defects was corroborated. The present reactive molecular dynamics study was focused on fusing temperature and a relationship between the fusing temperature and the number of interfacial dangling bonds was found which is shown in Figure 3.6. In details, I repeated the simulation procedure explained in Section 2.3.2 for the temperatures of 400, 600, and 700 K. As the diagram shows, the number of Ge dangling bonds at the GeO₂/Ge interface decreases when the fusing temperature increases. In particular, the simulated interface at 700 K brought about the lowest number of Ge interfacial dangling bonds. Hence, by regulating this parameter throughout the MOSFETs fabrication process, it can be inferred that the density of interfacial states could be significantly reduced.

This finding suggests a fabrication-level solution to reduce the interfacial states. Therefore, by increasing the temperature at which Ge is oxidized by O atoms – or is fused with the oxide layer similar to the present research – one is enabled to fabricate a more reliable Ge-MOSFETs.

Last but not least, with different cooling rate tested, I noticed that the faster the



Figure 3.6: The relationship between sputtering temperature and the number of dangling bonds at Ge/GeO₂ interface.

cooling rate, the higher the number of interfacial defects. By a higher cooling rate, while the computational cost increases, the interface become more uniform with less interfacial dangling bonds. On average, for the sample prepared at 500 K, the cooling rate of 2×10^{12} showed 25% less number of dangling bonds compared to the faster rate of 2×10^{14} . This finding indicates that if the structure cools down from a higher temperature quickly, the atoms get stuck in an unequilibrated energy level. Therefore, by lengthening the cooling process, one can ensure that atoms gradually reach the stable energy level, and, as a result, fewer interfacial defects will be achieved at the interface of GeO₂/Ge.

3.2 The Effect of Oxide Thickness on The Interfacial Defects

In this part, in order to investigate the effect of oxide thickness on the density of interfacial states, new sets of simulations were initiated. After preparing a new bulk of amorphous GeO_2 , the different thicknesses of amorphous GeO_2 were cleaved and placed on the Ge substrate as explained earlier in Section 2.3.2.

3.2.1 GeO₂ Structural Properties

Figure 2.5 shows the crystal of GeO_2 before heating and cooling process. In essence, to analyze the amorphous oxide, one needs to perform a coordination number¹ analysis for the system and examine if the coordination number of the involved atoms has changed after a certain period of time. Specifically, if the coordination number of the atoms has stabilized, it indicates that the system (the bulk oxide) has been randomized. Accordingly, an amorphous oxide, with eliminated grain boundaries, will be obtained. Figure 2.5 shows the structure of hexagonal GeO₂ before starting the heating process. In general, Ge atoms within a hexagonal GeO₂ have the coordination number of four, and that of oxygen atoms is two. However, due to cleaving the oxide, the atoms at the edges have some coordination number mismatches. As Figure 3.7 exhibits, before starting the simulations, there are some Ge atoms with the coordination number of one, two, and three. This is the case for O atoms as well, with some atoms with the coordination number of one, shown in Figure 3.8. Therefore, one should expect a minor error in the coordination number analysis of the bulk oxide, brought up due to these mismatches.

I analyzed the initial coordination number distribution of the system for the initially-prepared structure. Figure 3.9 represents the coordination number distribution of O and Ge atoms inside the bulk oxide when my system was about to endure the annealing process. This analysis was performed at different time steps to find out when the system reaches the steady state. Figure 3.10 and 3.11 exhibit the system coordination number distribution for the first and second half of the simulations. As Figure 3.10a illustrates, after minimizing the system's energy using an NVE ensemble, the average coordination number of Ge and O atoms become

¹The coordination number is abbreviated to CN in the insets.





(a) Under-coordinated Ge atoms with CN = 1.

(**b**) Under-coordinated Ge atoms with CN = 2.



(c) Under-coordinated Ge atoms with CN = 3.



close to theirs inside the hexagonal GeO_2 crystal (Ge = 4 and O = 2). The more the heating process proceeds, the more the coordination number changes. This trend continues until the coordination number of the involved atoms stabilizes. The insets in Figure 3.10 and 3.11 show the gradual change in the coordination number



Figure 3.8: O atoms with coordination mismatch at the edge of the simulation box due to cleaving. Ge = Green atoms, O = pink atoms, under-coordinated O atoms = red atoms.

distribution until reaching the equilibrium, when the distribution does not change considerably (Figure 3.11b, 3.11c, and 3.11d). This analysis reveals that within the amorphous structure I simulated using the force field developed by Ref. [45], Ge atoms tend to be fivefold coordinated, while O atoms are mostly twofold or threefold coordinated. It is worth noting that there are few Ge atoms to be fourfold and sixfold coordinated. To better clarify how Ge and O atoms are coordinated and bonded to each other, Figure 3.12 displays a slice section of the simulated bulk oxide with the thickness of 5 Å after pressure and temperature equilibration at 300 K and 1 atm at 680 ps.

As mentioned in Section 2.3.2, a higher temperature than GeO_2 melting point was chosen to heat up the oxide. At the end of cooling process and temperature/pressure equilibration, the RDF analysis of the bulk oxide was performed. The obtained structural properties of GeO_2 , illustrated in Figure 3.13, are summarized in Table 3.2. As represented in the Table, the results of the present work are in a close agreement with the literature. The sharp peak associated with each atom pair



Figure 3.9: The coordination number distribution of the initial structure shown in Figure 2.5, before starting the simulation.

in Figure 3.13 reveals the bond distance (bond lengths) between each atom pair. Therefore, the obtained Ge–O, Ge–Ge, and O–O bond lengths through this part of the work were 1.8, 3.2, and 2.8 Å. This is comparable with the experimental and simulation-based studies that are referenced in the Table 3.2.

The cut-off radii obtained from the RDF plot in Figure 3.13 was employed to calculate the nearest atom neighbours for each atom pair. Based on the collected cut-off radii, the average coordination number for each atom pair was obtained. As mentioned in Section 2.3.5, the integration around the first peak in Equation 2.7 provides the coordination number. Thereby, using the corresponding cut-off radius to each atom pair in Table 3.2, the average coordination number of Ge atoms with O atoms in the neighbourhood was 4.91, and that of O atoms with Ge atoms in the neighbourhood was 2.52 (Figure 3.11d). This value for Ge–Ge atom pair was 3.88 and that of O–O was 7.83. Besides Figure 3.11d, which represents the coordination number distribution within the bulk oxide, Figure 3.14 shows the MCN analysis for the bulk oxide at the last time step of the simulation, when the anneal-



after NVE, and before starting the annealing.

(a) The CN distribution of Ge and O atoms (b) The CN distribution of Ge and O atoms at timestep 500000.



(c) The CN distribution of Ge and O atoms (d) The CN distribution of Ge and O atoms at timestep 1500000. at timestep 100000.

Figure 3.10: The CN distribution of the involved atoms in the system during melting and cooling process within the first half of the simulation.

ing and temperature/pressure equilibration was finished and further confirms the average coordination number shown on Figure 3.11d for Ge and O atoms.

The average coordination number of Ge and O in the present work which was simulated with the ReaxFF developed in Ref. [66] is slightly higher than what reported previously. Basically, the pressure of the system affects how the involved atoms are coordinated. For instance, Ge atoms are sixfold coordinated with O atoms within a rutile structure which is a dense form of GeO₂. In this work, although there were not many Ge atoms with the coordination number of six, many of them had the tendency to be fivefold coordinated as represented in Figure 3.10 and Figure 3.11. Herein, unlike the previous studies [53, 60, 62] which did not con-



(a) The CN distribution of Ge and O atoms(b) The CN distribution of Ge and O atoms at timestep 2000000.(b) The CN distribution of Ge and O atoms







sider the effect of pressure in their simulations, I equilibrated the system at 1 atm and 300 K using the NPT ensemble at the end of simulation, and this is a reason for the slight difference.

3.2.2 Gate Oxide Thickness vs. Interfacial Defects

After preparing the bulk oxide, next, I cleaved the slices of the bulk oxide with the different thicknesses of 3, 4, 5, and 6 Å (e.g., Figure 3.12 for a five-angstrom sample) and sandwiched a Ge substrate between those slices. The system specifications described in Section 2.3.2. Given the structural properties found in Section 3.2.1,



Figure 3.12: Sliced section of the bulk oxide at 300 K and 680 ps with a slice depth of 5 Å. Ge = green atoms, O = red atoms.

when the heating, cooling, and final annealing processes finished, the prepared slabs were analyzed to determine the number of interfacial Ge dangling bonds. I found that smaller thicknesses of the oxide have a great impact on increasing the number of dangling bonds. However, once the oxide thickens, the number of dangling bonds at the interface decreases and that effect fades out. As is evident in Figure 3.15, for the thicknesses of 5 and 6 Å, the number of Ge dangling bonds are approximately the same, revealing that there is a limit in the relationship between these two quantities.

3.3 Ge Dangling Bond Types

I further investigated the types of Ge dangling bonds through the MD simulations. Figure 3.16 displays four different types of Ge dangling bonds observed in our simulations. Herein, those four types of Ge dangling bonds are named based on their oxygen back bonds. Based on the oxidation state, first, I denoted Ge^{0+} (Fig-

Atom Pair	Bond Length [Å]	Reference [Å]	cut-off Radius [Å]	$n_{lphaeta}$	Reference
Ge-O	1.8	1.75 [62], 1.73 [63, 64], 1.72 [53], 1.74 [65]	2.6	4.91	4 [62], 3.8 [63], 4.1 [53], 4.01 [65]
Ge–Ge	3.2	3.26 [62], 3.16 [63], 3.32 [53, 64], 3.25 [65]	3.6	3.88	4.1 [62, 63, 65], 4.4 [53]
0-0	2.8	2.84 [62], 2.83 [63], 2.81 [53, 64], 2.88 [65]	3.4	7.83	6.8 [62], 6.7 [63], 8.2 [53], 7.8 [65]

Table 3.2: The inter-atomic lengths of the atoms inside the bulk oxide, resulted from partial pair correlation function.

ure 3.16a), which is a threefold coordinated Ge atom and is only bonded to Ge atoms. Next, Ge¹⁺ (Figure 3.16b) and Ge²⁺ (Figure 3.16c) are threefold coordinated Ge atoms with one and two oxygen back bonds, respectively. Finally, Ge³⁺ (Figure 3.16d) which is bonded to three oxygen atoms. Evidently, rather than at the interface, Ge³⁺ is more probable to appear near the interface. The first-principles DFT study by Chang *et al* [67] showed that Ge⁰⁺ states are below the Fermi energy level and can act as Coulomb scattering centres for channel electrons and charge traps in n-MOSFETs. In addition, they reported that different Ge oxidation states that have no dangling bonds do not form any defect inside the Ge band gap. However, since Ge¹⁺ and Ge²⁺ generate energy states near the Conduction Band Minimum in Ge band gap, they cause electrical degradation. My results, which are in agreement with Ref. [67], suggest that Ge oxidation states that do not possess dangling bonds are not responsible for interfacial defects. However, Ge⁰⁺, Ge¹⁺, and Ge²⁺ generate energy band structure of Ge.



Figure 3.13: Radial Districution Function (RDF) of the bulk oxide at 300 K, at the end of the simulation (680 ps).

3.4 Dipole Effect

I also analyzed the charge distribution along the whole structure. This analysis revealed that there is a dipole layer near the interface of GeO_2/Ge . This finding is in line with the former study [67]. According to Ref. [67], the presence of oxygen vacancy inside the oxide network causes a positive fixed charge near the interface of gate oxide/substrate. This finding formerly reported for $\text{SiO}_2/\text{ZrO}_2$ [44] and $\text{SiO}_2/[\text{Al}_2\text{O}_3, \text{MgO}, \text{SrO}]$ [68]. As illustrated in Figure 3.17, the charge distribution of the involved atoms in the system described in Section 2.3.2 was plotted versus the length of simulation box along the Z direction in Cartesian coordinate system. The first two peaks wrapped around the plateau in Figure 3.17 are asso-



Figure 3.14: The Mean Coordination Number (MCN) analysis of germanium and oxygen.

ciated with two interfaces of GeO_2/Ge depicted in Figure 3.2. It reveals that there is a positive charge available near the interface at 65 Å (and 25 Å), followed by an equal magnitude but negative charge near 70 Å. This is happening mainly due to the higher electronegativity of O atoms compared to Ge. The existence of this dipole affects the threshold voltage of MOSFETs. Also, it can reduce the channel electron mobility as a result of Remote Coulomb Scattering (RCS) [69].

Although it is inevitable to have such an effect at the interface, there is a capacity and interest to study this effect further which is not the dedication of this research.



Figure 3.15: The relationship between the oxide thickness and the number of Ge dangling bonds at the interface of dielectric/substrate.

3.5 The Effect of Aluminum Doping on the GeO₂/Ge Interface Quality

In this section, the results of the system described in Section 2.3.4 will be presented.

The first observation of the structure analysis showed that although doped near the interface, Al atoms do not make bonds with Ge atoms at the interface of GeO_2/Ge . This observation validates why Ref. [70] had previously reported that Al atoms do not change Ge band gap after doping into GeO_2 .

The total number of defects analyzed in this part includes both interfacial and near-interface defects. The former are the defects that I figured out and depicted in Section 3.3, and the latter are basically Ge^{+3} , which are back bonded to three oxygen atoms, displayed in Figure 3.16d. Basically, Al atoms make bonds with O atoms near the interface. This bond formation leads to a decline in the number of



Figure 3.16: Types of Ge dangling bonds at GeO₂/Ge interface.

 Ge^{+3} because Al atoms bond to those Ge^{3+} and oxygen atoms. Therefore, those Ge^{3+} lose their dangling bonds as a result of bonding with Al and the oxide stabilizes. Figure 3.18 shows how Al content changes the total number of Ge dangling bonds by reducing the Ge^{3+} near the dielectric/substrate interface.

As depicted in Figure 3.18, there is a downward trend in the number of interfacial Ge dangling bonds; however, it does not necessarily guarantee that the more Al content, the less Ge dangling bonds. This is due to the fact that after the accumulation of Al atoms a new oxide layer of Al_2O_3 will be formed inside the GeO₂ as a segregated phase, and the reason why I doped dilute atomic concentrations of Al into GeO₂ structure lies in this fact. As mentioned in Section 2.3.4, for the case of yttrium, increasing the metal content resulted in the formation of a new conduction



Figure 3.17: Charge distribution along the length of simulation box displayed in Figure 3.2 along the Z direction.

path which is not desirable.

3.6 Dielectric Constant Calculation

The system specifications and simulation procedure of this section was explained in Section 2.3.3. As this and the next section are closely related, first, the calculated dielectric constants of different GeO_2 structures will be discussed here. Then, in the next section the effect of doping GeO_2 with Al atoms on the dielectric constant values will be discussed.

As explained earlier in Section 2.3.3, the dipole moments were collected within 10 ns through my MD simulations. Then, I plugged the values of the collected



Figure 3.18: Average number of interfacial Ge dangling bonds after Al doping, averaged over the last 50 ps of the simulation time span.

dipole moments in Equation 2.5. Table 3.3 represents the calculated dielectric constants (in this work and the literature) and density of different forms of GeO₂ for which I ran the MD simulations. To precisely simulate the ordered crystal structure of hexagonal GeO₂, NPT ensemble was utilized to retain the crystal structure of hexagonal GeO₂ intact at 300 K and 1 atm. This is because NVT ensembles do not consider the pressure of the system. Thus, as the system pressure increases, the crystal structure deforms and it cannot be considered as an ordered crystal of hexagonal GeO₂. Thereby, the dielectric constant of an alpha-GeO₂ was found to be 8.1 which is in compliance with claims in [6]. The results reveal that the closer to the crystal state, the higher the oxide dielectric constant. Thus, the amorphous GeO₂, which totally lost its crystal structure, possessed lower κ -value (5.6) than the hexagonal GeO₂ (8.1).

Structures	Density (g/cm^3)	Dielectric Constant (Literature)	Dielectric Constant (Current Work)
Tetragonal (rutile)	6.24	12 [6]	N/A
Hexagonal (alpha)	4.23	7[6]	8.1
Amorphous	3.63	5 - 5.9 [71, 72]	5.6

 Table 3.3: The dielectric constant of different GeO₂ structures.

As suggested in [55], dipole fluctuations can be used to calculate a material's dielectric constant. The dipole moment magnitudes and their distribution over the time duration of my simulations were analyzed for each structure. As is shown in Figure 3.19, the standard deviation of the dipole moments decreases when the oxide crystal structure deforms and changes to an amorphous oxide. Such behaviour led me to compare the κ -value of different samples which will be discussed further in the next section. It was observed that the decrease in the standard deviation of dipole moments results in lower permittivity. Therefore, as is evident from Figure 3.19, the hexagonal GeO₂ enjoys a higher dielectric constant compared to the amorphous GeO₂. Therefore, it can be inferred that the κ -value is greater for crystal structures; however, due to the nature of GeO₂ on Ge substrate, the growth of an amorphous oxide with lower permittivity near the interface is inevitable.

Since Sheikholeslam [44] reported earlier for Zr atoms within SiO₂, for the above-mentioned oxides, I further analyzed the relationship between the dielectric constant and coordination number of Ge atoms within the different oxide structures. It was discovered that the average coordination number of Ge atoms within all oxide structures are 5 ± 0.1 , indicating that there is not a sensible relationship between these two quantities in the present study.

3.7 The Effect of Aluminum Doping of GeO₂ on The Dielectric Constant

This section is focused on the impacts of Al doping into GeO_2 network. Given the improvement of the GeO_2/Ge interface quality after doping GeO_2 with Al atoms,



Figure 3.19: Average dipole moments distribution of different structures over the simulation period of 10 ns.

I also investigated the changes in κ -values after introducing Al atoms to the oxide structure. To that end, as explained earlier in Section 2.3.4, Al atoms were doped into the α -GeO₂ structure before forming the amorphous oxide. Then, the system went through all the similar steps of generating an amorphous GeO₂ which described in Section 2.3.2.

My samples constitute of 10 $(1.5 \text{ at. }\%)^2$, 15 (2.2 at. %), 20 (3 at. %), and 25 (3.8 at. %) Al atoms. I discovered that by introducing Al into the oxide structure, the dipole moments distribution changes. As is depicted in Figure 3.19, by increasing the Al content inside the oxide, the standard deviation of dipole moments distribution associated with each sample changes. The bell shape associated with each Al-doped oxide gradually becomes larger in width by increasing Al con-

²At. % stands for atomic percent.

Structures	Density (g/cm^3)	Dielectric Constant
Al-10 (1.5 at. %)	3.75	5.9
Al-15 (2.2 at. %)	3.74	6.2
Al-20 (3 at. %)	3.70	6.7
Al-25 (3.8 at. %)	3.69	7.4

Table 3.4: The dielectric constants of different Al-doped GeO₂.

tent. Therefore, as presented in Table 3.3, compared to amorphous GeO_2 with the dielectric constant of 5.6, Al-25 sample reached the high permittivity of 7.4. Comparing the Table 3.3 and Table 3.4 reveals that by increasing the Al content inside the oxide structure, the dielectric constant of the oxide increases.

Even though the sample with 25 Al atoms did not show a high κ -value as the high- κ oxide of Al₂O₃ with the dielectric constant of 10 to 10.37 [18, 71, 73], its κ -value becomes closer to the hexagonal GeO₂ with the κ -value of 8.1, calculated by my simulations.

Chapter 4

Conclusions and Future Work

4.1 Conclusions

Throughout this dissertation the current problems of Ge-MOSFETs were addressed by proposing several fabrication-level solutions, enabling experimentalists insight into what the causative agents for poor interface quality of GeO_2/Ge are. In addition, a novel approach for enhancing the gate oxide dielectric constant was proposed, which enhances the oxide/substrate interface quality at the same time.

First, I demonstrated the behaviour of Germania (GeO₂) when it reacts with a Ge substrate. I showed that GeO₂ has the tendency to deform to an amorphous structure on the Ge substrate, and it loses its crystallinity near the oxide/substrate interface. While a crystal GeO₂ possesses a higher dielectric constant, if possibly grown on the Ge substrate, due to having grain boundaries, Ge atoms diffuse inside the oxide and intermix with O atoms. This leads to the formation of Ge–O complex. On the other hand, although being beneficial due to having no grain boundaries, amorphous GeO₂ has a poor interface quality at the Ge substrate. Due to the intermixing of Ge atoms with O atoms inside the high- κ material, an amorphous GeO₂ will be grown on the Ge substrate. Therefore, removing the GeO₂ layer and growing a high- κ layer directly on the Ge substrate is impossible. As a result, to cope with the current reliability issues of Ge-MOSFETs, an efficient solution is to merely improve the interface quality of the dielectric/substrate.

Simulating the reaction of GeO_2 with the slab of Ge, led me to regulate the

fusing temperature at which GeO_2 reacts with the Ge substrate. Thereby, I showed that increasing the fusing temperature results in fewer Ge dangling bonds at the interface of oxide/substrate, revealing that the interface prepared at 700 K possessed the a fewest average dangling bonds of 6. Meanwhile, since thermal annealing is conventionally carried out as a part of semiconductors fabrication process in order to release the stress burdened to the system, on average, I noticed a 33% decline in the number of interfacial Ge dangling bonds. Accordingly, I conclude that the thermal annealing process further helps reach a more reliable device.

The device miniaturization is of paramount importance in electronics. MOS-FETs are not an exception and are shrunk in size. To that end, the need for a thinner gate oxide layer is inescapable. I first defined the structural properties of GeO₂, determined through employing reactive molecular dynamics force field (ReaxFF) developed by Ref. [45]. I investigated the extent to which the thinning of GeO₂ will damage the interface quality. My results unveiled that reducing the thickness of GeO₂ beyond 4 Å drastically increases the number of interfacial Ge dangling bonds. Thus, I determined the limit beyond which the quality of interface is damaged critically. Also, the established relationship between the oxide thickness and the number of Ge interfacial dangling bonds suggests that one cannot readily cover all the interfacial defects by merely growing a very thick layer of oxide.

In addition, as the reliability issues of Ge-MOSFETs stem from the Ge interfacial dangling bonds, I aimed for gaining an insight into their nature. Thus, the types of Ge dangling bonds were probed. Four types Ge dangling bonds were identified and characterized. While three types of Ge dangling bonds were identified at the interface, one type of them which I denoted as Ge^{+3} , was observed near the interface. Ge^{+3} mainly originates from the desorption of Ge–O from the interface. These defects are responsible for the dipole observed near the interface of GeO₂/Ge through this work. The observed dipole had been recognized earlier in [69] to affect the threshold voltage, and, also reduces the channel electron mobility. This issue requires further research.

Furthermore, I came up with a novel approach for improving the dielectric constant of gate oxide, while improving the interface quality. Starting off with calculating the dielectric constant of different crystal structures of GeO_2 , I simulated doping dilute concentrations of Al atoms into the GeO_2 dielectric layer. The rea-

son why denser Al contents were not doped into the oxide was to avoid a phase segregation within the oxide layer.

First, to analyze the effect of Al doping on the interface quality, I introduced Al atoms to the oxide layer of GeO₂/Ge structure. The idea of introducing metals to the oxide network originated from the previous studies for reducing the water-solubility of GeO₂. One can dope metals into the oxide network to make it more robust. The robustness of the oxide network refers to the enhancing effect of the Y^{3+} cation which bonds to the nearest oxygen atoms inside the oxide structure and strengthens it. Thereby, I analyzed the simulated oxide/substrate structure and found that Al doping results in a drop in the number of interfacial defects due to reducing the number Ge⁺³ defects identified in my work. By increasing the Al content, the results revealed an improving trend in reducing the number of Ge dangling bonds. However, this trend does not guarantee that by doping more Al into the oxide, one can acquire a perfect dielectric/substrate interface without interfacial defects. The reason is that due to the formation of an inner Al₂O₃ layer, GeO₂ will finally segregate from Al₂O₃ and a layer with its own defects will be formed again.

Next, to find out how the Al doping affects the dielectric constant, I first calculated the dielectric constant of GeO_2 and compared my results with the literature to validate the followed procedure. While due to the force field limitation I could not calculate the κ -value of the dense form of GeO₂ (rutile Germania), my results for hexagonal and amorphous structure were in a close agreement with the literature. Therefore, different samples with dilute concentrations of aluminum were prepared. Besides the previous finding with respect to interface quality improvement, I observed that Al doping also improves the dielectric constant of GeO_2 . In detail, I collected the dipole moments of the system to calculate the dielectric constant. Accordingly, the dipole moments distributions were analyzed for all the samples. Evidently, the deviation of associated plot to each sample in Figure 3.19 altered depending on the amount of Al content. I noticed the larger the deviation of each graph, the higher the dielectric constant, establishing the sample with 25 Al atoms to have a high κ -value of 7.4. While this value is not yet as high as that of Al₂O₃, which is a high- κ oxide with the κ -value of 10 to 10.37, reaching a comparable result to the κ -value of hexagonal GeO₂ (8.1) was worthwhile.

This research enables R&D experts to improve the interface quality of GeO_2/Ge by regulating the gate oxide thickness and oxidation temperature of Ge during the Ge-MOSFETs fabrication. Moreover, I suggested a novel approach which not only helps decrease the number of interfacial defects, but also enhances the dielectric constant of the gate oxide in Ge-MOSFETs. Specifically, the Al doping into the molecular structure of GeO₂ boosts the dielectric constant of the simulated GeO₂ gate oxide layer in this work.

4.2 Future Work

The possibility of expanding this research for determining a new dielectric material with a high dielectric constant and interface quality on the germanium substrate exists. If the proper force field were developed, there is the possibility of simulating $Ge/GeO_2/Al_2O_3/HfO_2$ gate stack. The approach I took to compute the dielectric constant enables researchers to study the dielectric properties of the Al_2O_3/GeO_2 layer, which previously simulated by Ref. [45] and was not studied in my work. To gain more insight into the dielectric behaviour of GeO_2 and/or metal-doped GeO_2 structures, the effect of changing the temperature on the dielectric constant can be simulated using my approach in this study. Also, studying the dipole effect observed in this research is pivotal because it changes the threshold voltage of MOSFETs and affects the device performance.

There are also other metals that have the potential of stabilizing GeO_2 gate oxide. Yttrium is one of the metals highly recommended to drastically improve the gate oxide reliability. Therefore, the procedure I took for carrying out the simulations will help scientists to study how the interface quality of the oxide/substrate changes by doping other metals into GeO_2 . In addition to investigating the interface quality of yttrium-doped GeO_2 , one can study the dielectric property of the yttrium-doped GeO_2 .

Since Ge is not as abundant as Si, Ge channels are integrated on Si substrates in order to utilize less Ge as the substrate material. Accordingly, the relationship between the gate oxide thickness and the thickness of the Ge layer integrated on the Si layer can be studied. Thus, the interface quality of oxide/substrate in such MOSFETs can be simulated as well.

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