ATOMISTIC-SCALE INVESTIGATION OF THE GROWTH KINETICS OF
ALUMINUM OXIDE LAYERS ON ALUMINUM NANOPARTICLES AND
GERMANIUM-BASED SEMICONDUCTORS USING THE REAXFF REACTIVE
FORCE FIELD

A Dissertation in
Mechanical Engineering
by
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Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

August 2016
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ABSTRACT

In this dissertation, the ReaxFF potential was employed to investigate the complex surface chemistry of two nano-scale systems, including growth of aluminum oxide (Al$_2$O$_3$) layers on aluminum nanoparticles (ANPs) and Ge-based semiconductors. ANPs have been considered “energetic materials” due to their high enthalpy of oxidation and potentially applicable to rocket propellant formulations. In addition, there is a growing interest in using the Ge-based semiconductors to replace conventional Si-based semiconductors. However, a quantitative and comprehensive understanding of kinetic mechanisms associated with the above-mentioned systems has not yet been fully achieved, primarily due to complexities of their reaction processes in nature. Given this, the present work is motivated by two research questions: (1) What are the dominant factors that give a higher degree of energy efficiency during the oxidation process of ANPs, and (2) What is the optimal guidance for manufacturing Ge-based semiconductors? As such, this study aims to gain atomistic-scale insights into growth kinetics of passivation layers on ANPs and Ge surfaces using the ReaxFF reactive force field method. To achieve these aims, research strategies included: (a) application of the ReaxFF potential for Al/O system being chosen as a means of understanding the mechanism of the oxidation of ANPs; (b) development and application of a ReaxFF reactive force field for Al/C/H/O interactions to study the effects of surface modification on the oxidation kinetics of the ANPs; and (c) extension of the ReaxFF potential to Ge/Al/C/H/O systems to directly model an Al$_2$O$_3$ atomic layer deposition (ALD) process on Ge surfaces, and comparing computational results with experimental work. Our findings from combined ReaxFF and experimental studies offer very promising options and systematic strategies for the ANPs and the Ge-based semiconductors to be used in the combustion and the ALD applications, respectively. In summary, this dissertation clarifies mechanisms for growth kinetics of passivation layers (i.e., Al$_2$O$_3$ layer) on ANPs and Ge surfaces and suggests
future directions for studying the reaction kinetics of a wide range of complex nano-scale systems from an atomistic-scale viewpoint.
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ACKNOWLEDGEMENTS

First of all, I would like to express my deepest gratitude to my advisor, Dr. Adri van Duin, for the past four years during my Ph.D. program at the Pennsylvania State University. He has always provided wonderful and beautiful ideas when I have faced any trouble and difficulties on my research projects, and consequently I would be able to develop my potential ability to construct research ideas independently. With his guidance and intuition, it would also be made possible to gain comprehensive insight into atomistic-scale simulations, helping me conduct advanced research topics. I have really enjoyed my Ph.D. program as working with him, and learned how to collaborate with experimentalists. These factors definitely make me to be more confident on my research ability for my next career. I would also like to thank Drs. Yetter, Xuan, and Engel-Herbert for serving on my Ph.D. committee.

I would greatly appreciate my previous advisor, Dr. Junemo Koo, during my Master's study at Kyung Hee University. Without his unconditional support and guidance, I would never have imagined pursuing a high level of degree. I was able to have fundamental ideas about how to do “Research” and how to analyze “Raw data”, enabling me to get a solid background for my research ability. I believe my passion for research should be motivated by his kind and nice attitude toward his students.

I should mention my wife, Jiwon Hwang, in this acknowledgements. She has been not only my lovely wife, but also the best colleague, advisor, and even “competitor”. We have always studied at the Pattee library, sitting definitely next to each other, and having same coffee, lunch, and dinner for the past three years. This indicates that we have never been separated to each other during the whole day except for a meeting with others. Although we have a different background - I am majoring in mechanical engineering while she is majoring in special education, that doesn’t matter; we have extensively discussed our research contents, and sometimes toughly critiqued our
research analyses for a high quality of research paper. Without hesitation, these steps obviously allow us to become a good researcher, and also communicate with other researchers with more confidence.

I would like to thank my lab members and colleagues during my Ph.D. study. Especially, I have learned about basic MD skills with the help of Dr. Yun Kyung Shin, and enjoyed comprehensive and valuable discussion with Mahbub, Chowdhury, Jonayat, and Kichul. In addition, I have really enjoyed my research by collaborating with Yuanxia Zheng, a Ph.D. student in Dr. Engel-Herbert group.

I would like to thank my parent and sister, and I would greatly appreciate my parent-in-law, Dr. Seok Yoon Hwang, and Eunhi Cha for their supports and love. I would be able to enjoy my research during my Ph.D. program with the help of their encouragement. In addition, I have enjoyed with KakaoTalking my sister-in-law, Jiyung Hwang, and brother-in-law, Taeseung Hwang for sharing our dynamic life.

Finally, I will continue my research career at the University of Southern California as a postdoctoral scholar - research associate. I am very excited with continuing my research with new mentor and colleagues. Please pray for my next career. Thank you.
Chapter 1

Introduction

Growth of aluminum oxide layers has been widely investigated in several scientific areas, ranging from thermal oxidation on aluminum nanoparticles (ANPs) to thin-film deposition on semiconductors.\textsuperscript{1-4} The formation of an aluminum oxide layer on ANPs has attracted particular attention in the combustion community because bulk aluminum has a high enthalpy of oxidation related to the following chemical equation:

\[
\text{Al (bulk) + O}_2 \rightarrow \text{Al}_2\text{O}_3 \text{ (S)} \quad \Delta H_{\text{bulk}} = -400 \text{ kcal/mol}
\]  

(1)

It is noteworthy that nano-scale aluminum particles are found to be more reactive (\textit{i.e.}, faster energy release) than larger-scale particles,\textsuperscript{5} primarily due to a higher specific surface area, giving them greater application in solid propellants and explosives.\textsuperscript{6-9} While ANPs have these useful properties for solid particle fuels (see Figure 1-1), they also have a limitation in this application due to the oxide layer on ANPs that naturally forms prior to the combustion process.\textsuperscript{10} That is, the oxide layer on ANPs that rapidly forms at low temperature is a major issue since it does not contribute to the high energy release of metal particles but rather functions as dead weight. For this reason, alternative protective layers that overcome the drawback of the oxide layer have been suggested, including transition metal, noble metals, and some organic coatings.\textsuperscript{10-14} Consequently, it is essential to understand the oxidation process of surface-protected ANPs (as compared to bare ANPs) for use as possible ingredients of reactive additives.

On the other hand, the formation of an aluminum oxide layer on ultrathin substrates, such as a \text{Al}_2\text{O}_3/\text{GeO}_x/\text{Ge} gate stack,\textsuperscript{15} is of particular interest recently in the semiconductor industry because the aluminum oxide layer is known to have thermal/chemical stabilities, good adhesion to most surfaces, and excellent dielectric properties.\textsuperscript{16-17}
Figure 1-1. (a) Schematic of the solid fuel rocket. The solid fuel and oxidizer are mixed in the propellant grain and (b) TEM image of growth of aluminum oxide layers on ANPs during oxidation.\textsuperscript{5}

Figure 1-2. (a) Schematic of the high-$\kappa$/Ge gate stack and (b) TEM image of the multi-interlayer high-$\kappa$/AlO$_x$/GeO$_x$/Ge gate stack.\textsuperscript{18}

Consequently, the aluminum oxide layer has been considered as a suitable material for an interface layer (IL) between the high-$\kappa$ gate dielectric and the GeO$_x$/Ge gate stack as shown in Figure 1-2. In order for the aluminum oxide film to be deposited on the GeO$_x$/Ge substrate, an atomic layer deposition (ALD) process, using trimethylaluminum (TMA) and water cycles, has been employed since this technique enables a very uniform aluminum oxide layer to be obtained with an accurate atomic-layer scale control.\textsuperscript{19} As a result, understanding the deposition process of the aluminum oxide layer on the Ge substrate is the key to high-$\kappa$/gate stack applications.
However, the growth kinetics of the aluminum oxide layer on untreated/surface-modified ANPs and Ge-based semiconductors have not been completely understood. In addition, the surface chemistry of such interactions is not yet clear. Therefore, the primary aims of this work are to investigate the effects of surface modification on the oxidation kinetics of ANPs and to elucidate the thin film deposition process on the Ge substrate using the Al₂O₃ ALD. For these purposes, the ReaxFF reactive force field was employed, which enables us to gain insight into the formation of the aluminum oxide layers on nano-scale materials from an atomistic-scale point of view and at relatively low computational costs when compared to ab initio calculations. Chapter 2 provides brief descriptions of classical molecular dynamics (MD) simulations and the ReaxFF reactive force field method. The growth kinetics of aluminum oxide layers on bare and surface-modified ANPs are examined in the Chapters 3 and 4, respectively. Chapter 5 investigates the growth kinetics of the aluminum oxide layer on the Ge-based semiconductors. Finally, Chapter 6 provides conclusions drawn from the present study.
Chapter 2

Research Methods

2.1 Molecular Dynamics (MD) Simulations

MD simulation is a computational method used to solve a many-body problem using Newton's equation of motion as shown in Equation (2); a basic assumption of the MD simulation is that trajectories of atoms and molecules can be described in the classical Newtonian dynamics:\(^2\)

\[ F_i(t) = m_i \frac{d^2 r_i(t)}{dt^2}, \quad i = 1, 2, \ldots, N \]  

(2)

where \( m_i \) is the mass of the \( i \)th atom, \( r_i(t) \) is the position vector of the \( i \)th atom, and \( F_i(t) \) is the force acting on the \( i \)th atom at time \( t \). For numerical calculations, the second-order differential terms in the equation of motion should be time-discretized. This numerical integration can be achieved by well-established algorithms such as the Verlet algorithm.\(^3\) In the Verlet algorithm, the atoms' positions are calculated as shown in Equation (3)

\[ r_i(t + \Delta t) = 2r_i(t) - r_i(t - \Delta t) + \frac{F_i(t)}{m_i} \Delta t^2 + O(\Delta t^4) \]  

(3)

As indicated, the Verlet algorithm is known to be simple and stable (the global error of the Verlet algorithm is on the order of 4); however, velocity vectors, \( v_i(t) \), are not explicitly obtained from the Verlet algorithm. The velocity could be obtained by a central difference formula in Equation (4), but this scheme gives rise to the global error on the order of 2.

\[ v_i(t) = \frac{r_i(t+\Delta t) - r_i(t-\Delta t)}{2\Delta t} + O(\Delta t^2) \]  

(4)
To resolve such a problem, the Velocity Verlet scheme has been developed: the atom's positions are calculated, and the atoms' velocities are explicitly propagated at the same time $t$ as follows:

$$r_i(t + \Delta t) = r_i(t) + v_i(t)\Delta t + \frac{F_i(t)}{2m_i} \Delta t^2 + O(\Delta t^3)$$  \hspace{1cm} (5)

$$v_i(t + \Delta t) = v_i(t) + \frac{\Delta t}{2m_i} [F_i(t + \Delta t) + F_i(t)] + O(\Delta t^3)$$  \hspace{1cm} (6)

The atoms' positions and velocities can be calculated at the same time $t$, and the global error in the Velocity Verlet algorithm is on the order of $3$. Because of these advantages, the Velocity Verlet scheme has been implemented in the ReaxFF-MD algorithm. A general algorithm for MD simulations is summarized in Figure 2-1. Further information on the MD algorithms can be found in the References.\textsuperscript{24-25}

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**Figure 2-1.** A general algorithm for MD simulations
2.2 The ReaxFF reactive force field method

Basically, the force acting on the $i^{th}$ atom can be obtained by the first derivative of interatomic potentials (i.e., a force field), $U(r_1, ..., r_N)$, with respect to atomic displacement, as shown in Equation (7).

$$
F_i = -\left( \frac{\partial U}{\partial x_i}, \frac{\partial U}{\partial y_i}, \frac{\partial U}{\partial z_i} \right)
$$

Thus, the reliability of the MD simulations mostly depends on how exactly the force field describes the characteristics of physical models. In other words, the force field should correctly mimic the physical behaviors of the complex chemical systems being examined. Given these circumstances, the ReaxFF reactive force field has been developed for a wide range of chemical systems, including hydrocarbon/oxygen interfaces, silicon/silicon dioxide interfaces, aluminum/aluminum oxide interfaces, aluminum hydrides, nickel/hydrocarbon interactions, and titanium dioxide/water interactions. Furthermore, it has been demonstrated that the ReaxFF potential can predict the characteristics of such chemical systems successfully.

The ReaxFF reactive force field is an empirical force field mainly derived from a quantum mechanics (QM)-based parameterization. ReaxFF uses a bond order/distance relationship introduced by Tersoff that was firstly applied to carbon systems by Brenner. Because the bond order is calculated from the bond distance and updated at every step, ReaxFF essentially does not use a rigid connectivity for atoms in the system, making it possible to describe chemical reactions (i.e., breaking and forming bonds). For example, as shown in Figure 2-2, reporting a C-C bond order as a function of a bond distance, ReaxFF captures the bond order of three at the shortest distance, while ReaxFF calculates the bond order of zero at an infinite distance. Because such a description consists of a continuous function, ReaxFF has the ability to describe a smooth transition from non-bonded to single-, double-, and triple-bonded systems robustly. This is the primary reason why ReaxFF can describe reactive events during MD
simulations. The general expression for total energy shown in Equation (8) is used to describe the ReaxFF reactive force field:

\[
E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{tp}} + E_{\text{val}} + E_{\text{tors}} + E_{\text{vdWaals}} + E_{\text{Coulomb}}
\]  

(8)

The total energy term \((E_{\text{system}})\) contains the bond energy \((E_{\text{bond}})\), over-coordination \((E_{\text{over}})\), under-coordination \((E_{\text{under}})\), lone-pair \((E_{\text{tp}})\), valence angle \((E_{\text{val}})\), torsion angle \((E_{\text{tors}})\), van der Waals \((E_{\text{vdWaals}})\), and Coulomb \((E_{\text{Coulomb}})\) energy. The bond order is directly calculated from the interatomic distance and updated every iteration for all bonded interactions, including covalent bonds, valence, and torsion angles.

Figure 2-2. A C-C bond order as a function of interatomic distance\(^{21}\)

In addition, ReaxFF also describes non-bonded van der Waals and Coulomb interactions. Such interactions are calculated for all pairs of atoms (i.e., no exclusions) and extremely short-range interactions are dampened by using shielding terms. Polarization effects are considered by using a geometry-dependent charge distribution derived from an electronegativity equalization method.\(^{34}\) Further details concerning the description of ReaxFF are available in van Duin et al.\(^{20}\).
The history of the ReaxFF formalism and its development can also be found in a recent ReaxFF review paper.  

2.3 The ReaxFF reactive force field optimization

ReaxFF reactive force field parameters are generally obtained by using a well-established one-parameter search method described by van Duin et al. In order to optimize the ReaxFF parameters for comprehensive chemical systems, including Al/C/H/O and Ge/Al/C/H/O interactions, QM calculations have been carried out for both periodic and non-periodic systems. The ReaxFF parameters were then fit against those from the QM-based training sets to reduce the total error, as shown in Equation (9):

$$ \text{Error} = \sum_{i=1}^{n} \left( \frac{x_{i,QM}-x_{i,\text{ReaxFF}}}{\sigma} \right)^2 $$

where $x_{i,QM}$ and $x_{i,\text{ReaxFF}}$ indicate the values of the QM and the ReaxFF calculations, respectively. Generally, equations of states (EOS), heats of formation, reaction energies, bond dissociation energies, angle distortion energies, and geometries of molecules (bond lengths and angle) are included in the ReaxFF training set. During the ReaxFF force field optimization, all initial structures derived by the QM calculations were fully relaxed with certain bond/angle restraints and/or fixed layers. The order of each ReaxFF parameter optimized was not fixed but dynamically decided by how the current ReaxFF parameters quantitatively mimic the QM data points being examined. For example, if the current ReaxFF description was not able to reproduce a full bond dissociation curve (e.g., a Al-C bond) correctly, then a relatively small number of $\sigma$ in Equation (9) for several data points, including Al-C bond energies with bond restraints, were assigned, and the force field training scheme primarily focuses on optimizing Al-C bond parameters and/or Al-C off-diagonal parameters. As a result, the total error of the training set
becomes sensitive on the data points that hold a relatively small number of $\sigma$ \textit{i.e.}, Al-C bond dissociation energy in this case), and, consequently, Al-C bond and off diagonal-related parameters can be optimized to correctly describe the Al-C full bond dissociation curve.

Additionally, while the quality of the ReaxFF description can be enhanced by adding a large number of QM data points in the training set, it would also make the force field training non-trivial. This is because the order of optimizing ReaxFF parameters and the weight number should be monitored and re-assigned based on how the total error of the training set changes at the end of a single cycle of the one-parameter search scheme. As such, Chapters 4 and 5 report the extent of QM calculations for the ReaxFF training set and ReaxFF parameters' fits to the QM calculations, aiming to develop ReaxFF parameters for both Al/C/H/O and Ge/Al/C/H/O interactions.
Chapter 3

Growth kinetics of aluminum oxide layers on bare aluminum nanoparticles

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3.1 Introduction

As introduced in Chapter 1, aluminum nanoparticles (ANPs) have been considered as a solid propellant in the application of solid-fuel rockets because of their high combustion enthalpy, low cost, and environmentally-safe combustion products.\textsuperscript{38-39} In addition, ANPs have a much greater surface-to-volume ratio than larger particles (e.g., micron-size particles), resulting in relatively high chemical reactivity, low melting temperatures, and high energy density.\textsuperscript{40-41} Consequently, there has been increasing interest in using ANPs as a fuel in the combustion community.\textsuperscript{6-8} It is of particular interest to elucidate a mechanism of the oxidation of the ANPs, because their high-energy characteristic is the results of an oxidation process. For this reason, many researchers have extensively studied the oxidation process of the ANPs. Table 3-1 presents a list of previous experimental and theoretical studies of the oxidation kinetics of aluminum materials.\textsuperscript{5, 42-50} For example, Jeurgens \textit{et al.}\textsuperscript{42} conducted an experimental study of the growth of the oxide film on a bare Al(4 3 1) substrate. They reported that the oxidation stages can be divided into two regimes, \textit{i.e.}, 1) the initial rapid oxidation and 2) the second slow oxidation, and they concluded that the two different rates of oxide film growth resulted from an outward transport of Al cations and the inward diffusion of O anions, respectively. Additional
experimental studies were conducted to demonstrate the mechanism of the oxidation of the ANPs. Rai et al.\textsuperscript{5} suggested that a slow oxidation process occurs below the melting point of aluminum through the diffusion of oxygen and that rapid oxidation occurs above the melting point through the diffusion of both oxygen and aluminum, which increases the oxidation rate. Similar results were reported by Hasani et al.\textsuperscript{44} They suggested that the oxidation of aluminum powder occurs in three different stages. They concluded that slow oxidation occurred in the first stage because an initial, amorphous oxidation crust protected the metal aluminum below this crust. At temperatures up to 873 K, the rate of the oxidation increased as the amorphous oxidation crust was changed into a crystalline phase. However, as the temperature increased up to 973 K, the rate of the oxidation decreased because the diffusion paths of oxygen were blocked by the continuing oxidation process. Furthermore, computational approaches have been employed to demonstrate the kinetics of the oxidation of ANPs. Clark et al.\textsuperscript{47} performed molecular dynamic (MD) simulations of the oxidation of ANPs and identified three stages in the oxidation state of the ANPs initiated by heating. They specifically employed an embedded atom method (EAM) potential for the aluminum bulk metal\textsuperscript{51} and a bond-order coupling scheme\textsuperscript{52} for aluminum/oxygen interactions. At the confined heating stage, the oxygen diffusion across the metal boundary was dominant. As the rate of heating increased, the rate of oxygen uptake increased due to the melting of the alumina shell. Subsequently, direct oxidation occurred through the ejection of aluminum atoms into the surrounding oxygen. Campbell et al.\textsuperscript{48} also utilized MD simulations of the oxidation of a bare aluminum cluster with a diameter of 20 nm, which is based on electro static plus (ES+) potential\textsuperscript{53}. They reported that the oxide layer was developed by large pressure variations in the oxide layer, which caused a rapid diffusion of Al atoms to the surface and O atoms to the interior of the cluster. Henz et al.\textsuperscript{49} used ReaxFF-MD simulations of the oxidation of ANPs that had an oxide layers that were 1 and 2 nm thick, and they concluded that the high level of the diffusion of aluminum atoms during the oxidation was caused primarily by
an induced electric field in the oxide layer. In summary, the growth of the oxide layer on ANPs has been attributed to the combined effects of the expansion of the volume of aluminum atoms and the inward diffusion of oxygen atoms.

Table 3-1 Examples of previous studies on the oxidation kinetics of aluminum materials

<table>
<thead>
<tr>
<th>Author</th>
<th>Materials</th>
<th>Methods</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jeurgens et al.</td>
<td>Al (4 3 1) slab</td>
<td>X-ray photoelectron spectroscopy</td>
<td>Kinetics of the growth of oxide film as a function of temperature</td>
</tr>
<tr>
<td>Hunter et al.</td>
<td>Al cluster</td>
<td>Electrical arrangement for determining barrier layer thickness</td>
<td>A rate of formation of naturally and thermally formed oxide films on aluminum materials</td>
</tr>
<tr>
<td>Rai et al.</td>
<td>ANPs</td>
<td>TEM micrographs</td>
<td>The mechanism of the oxidation of ANPs</td>
</tr>
<tr>
<td>Hasani et al.</td>
<td>ANPs</td>
<td>TG-DTA thermal analysis</td>
<td>The mechanism of the oxidation of ANPs</td>
</tr>
<tr>
<td>Chung et al.</td>
<td>ANPs</td>
<td>Theoretical model</td>
<td>The enthalpy of oxidation of ANPs as a function of particle diameter</td>
</tr>
<tr>
<td>Cai et al.</td>
<td>Al (1 1 1) slab</td>
<td>X-ray photoelectron spectroscopy</td>
<td>The effect of the pressure of oxygen gas on the oxidation kinetics</td>
</tr>
<tr>
<td>Clark et al.</td>
<td>ANPs with a hollow amorphous alumina shell</td>
<td>Multimillion-atom reactive molecular dynamics simulations</td>
<td>Three stages in the initiation of ANPs due to heating</td>
</tr>
<tr>
<td>Campbell et al.</td>
<td>ANPs</td>
<td>Molecular dynamics simulations</td>
<td>The structural and dynamic correlations in the oxide region and evolution of charge, oxide thickness, diffusivities of atoms, and local stress</td>
</tr>
<tr>
<td>Henz et al.</td>
<td>ANPs with 1 nm and 2 nm thick oxide layer</td>
<td>ReaxFF-molecular dynamics simulations</td>
<td>Mechanism of the oxidation of ANPs</td>
</tr>
<tr>
<td>Hasnaoui et al.</td>
<td>Al surface at low index</td>
<td>Molecular dynamics simulations</td>
<td>The effects of the temperature and oxygen pressure on the oxidation kinetics</td>
</tr>
</tbody>
</table>
The driving forces for such kinetics can originate from the temperature of the system, the pressure of the oxygen gas, pressure variations in the oxide layer and/or the induced electric filed through the oxide layer.

However, the effects of the system temperature and oxygen gas pressure on the oxidation of ANPs are not fully understood. Also, a detailed analysis of the oxidation states of the ANPs during the oxidation process, i.e., a transition from metal to metal oxides is missing. Thus, Chapter 3 aims to investigate how temperature controls the growth of the oxide layer on the ANPs and to analyze the oxidation states of the ANPs in terms of metal, sub-oxide, oxide, and super-oxide. To achieve those aims, the ReaxFF reactive force field was used to examine Al/O interactions from an atomistic-scale perspective. Thus, this study deals with the ReaxFF-MD simulations of the oxidation of a bare Al substrate for validating the current ReaxFF description and the oxidation of ANPs in order to understand the mechanisms by which the oxide layer grows.

3.2 Computational details

![Figure 3-1. System configurations: (a) 504 Al-atoms of the Al (4 3 1) slab; (b) 864 Al-atoms of the ANPs](image)
To validate the current ReaxFF description and apply it to the Al/O systems, two structures were prepared as follows: 504-Al atoms of Al (4 3 1) slab (1.40 \times 1.28 \times 4.82 \text{ nm}) (see Figure 3-1a); and 864-Al atoms of an amorphous Al cluster (diameter of 2.8 nm) (see Figure 3-1b). The system configurations were displayed by the Visual Molecular Dynamics (VMD) molecular graphics viewer,^54^ Visiit,^55^ and Molden. The slab was built by cleaving the (4 3 1) plane of fcc-Al crystal and then placing the slab in a 1.4 \times 1.28 \times 10.0 \text{ nm} simulation box with 150 oxygen molecules. The amorphous cluster was obtained by annealing the fcc-Al crystal containing 864 A­l-­atoms from 0 to 800 K for two cycles. Then, the annealed cluster was placed in the middle of a simulation box that measured 5.0 by 5.0 by 5.0 nm. Two different number of oxygen gas, i.e., 300 and 600 oxygen molecules, were distributed randomly in the simulation box with a periodic boundary condition, corresponding to oxygen gas densities of 0.13 and 0.26 g/cm^3, respectively. In order for the ReaxFF-MD simulations to deal with chemical reactions to occur smoothly, it has been reported that the time step needs to be lower than 1 order of the highest frequency of molecules (generally t \sim 0.5 to 1.0 \text{ fs}).^26^ In this study, the system temperature were controlled up to 900 K, and it was found that the time step of 0.2 fs efficiently describes the adsorption, dissociation, and diffusion of oxygen molecules. Hence, all the simulations were performed with a time step of 0.2 fs and 5,000,000 iterations (up to 1.0 ns). Since this study was focused mainly on the oxidation of ANPs as a function of the temperature of the system, it was essential to control the temperature of the system during the MD simulations. For this reason, a canonical ensemble was used, i.e., a constant number of atoms, constant volume, and constant temperature. In the canonical ensemble, a variety of thermostatic methods were used to control the temperature of the system, such as Nose^57/ Hoover^58^, Berendsen,^59^ and Anderson. It has been suggested that the Nose/Hoover thermostat correctly describes the canonical ensemble with true dynamics, because such method makes it possible to obtain a canonical distribution of the particles’ positions and momenta by using the extended Hamiltonian system.^61^ Hence, it was
chosen to use the Nose/Hoover thermostat with a temperature damping constant of 100 fs implemented on the 29 Jan 2014 version of LAMMPS code.\(^6\) In addition, the 864-atoms of the ANPs was heated up from 0 K to 1000 K with a heating rate of 0.02 K/fs to evaluate the melting temperature of the ANPs using the current ReaxFF description. The melting temperature of the 864-atoms of the ANPs is found to be \(\sim 800\) K.

### 3.3 Results and discussion

#### 3.3.1 Validation of the ReaxFF reactive force field for the oxidation of ANPs

![Figure 3-2. Initial configuration of the Al (4 3 1) slab with 150 oxygen molecules: The silver color represents an aluminum atom, and the red color represents an oxygen atom.](image)

To validate the existing ReaxFF description for the Al/O interactions, ReaxFF-MD simulations of the growth of an oxide film on an Al (4 3 1) substrate were carried out, which was previously conducted by an experimental study.\(^4\) The experimental study was carried out with a very low oxygen gas pressure (initial oxygen density of \(\sim 1.37 \times 10^{-12} \text{ g/cm}^3\)), and it was found
that the amorphous oxide layer attained a limiting thickness at a low temperature (T ≤ 573 K), whereas at high temperature (T < 573 K), the growth of the oxide layers was not impeded by the limiting thickness. Thus, the present study evaluated if the ReaxFF reactive force field could correctly reproduce the trend of dependence on temperature in the growth of the aluminum oxide film. Figure 3-2 shows the initial configuration of the Al(4 3 1) slab with 150 oxygen molecules. To demonstrate the effects of the temperature of the system on the growth of the oxide film on the Al(4 3 1) slab, ReaxFF-MD simulations were performed at 473 K, 573 K, and 673 K. However, it is impractical to perform the MD simulations up to the time scales used in the experimental approach (e.g., t > 1.0 s) because of limitations of the time step and the computational cost.\textsuperscript{63-64} Hence, the ReaxFF-MD simulations were performed with relatively high oxygen gas pressure (initial oxygen density of 0.48 g/cm\textsuperscript{3}) to describe the growth of the oxide film up to the limited time scale (t ~ 1.0 ns). Then, the growth of the oxide film in the ReaxFF results were compared with the experimental data.

Figure 3-3. Final snapshots (t = 1.0 ns) of the oxide-film on the Al(4 3 1) slab: (a) at 473 K; (b) at 573 K; (c) at 673 K. Yellow lines represent the aluminum/aluminum oxide interfaces
The final snapshots (t = 1.0 ns) of the Al(4 3 1) substrates at 473 K, 573 K, and 673 K are shown in Figure 3-3a, 3-3b, and 3-3c, respectively. The amorphous aluminum oxide films developed on the Al(4 3 1) substrates during the thermal oxidation process, and it was clear that the thickness of the aluminum oxide film increased as the temperature increased. Figure 3-4 compares the growth of the oxide film as a function of time in the computational and experimental approaches. It is apparent that the oxide film reached a limiting thickness at low temperature (T ≤ 573 K) at t ~ 0.5 ns, whereas the thickness increased continuously at high temperature (T = 673 K) up to t = 1.0 ns. Therefore, it was demonstrated that the ReaxFF qualitatively predicted the characteristics of the oxidation of the aluminum material with respect to the temperature of the system.

Figure 3-4. Comparison of the growth of the oxide film as a function of time in the ReaxFF and experiment.\textsuperscript{42}
3.3.2 The mechanism of the oxidation of the ANPs

In order to verify how temperature controls the growth of the oxide layer on ANPs, temperature distributions on cross sections of the ANPs and effects of these distributions on the growth of the oxide film were investigated. Figure 3-5a-b show the initial configurations of the ANPs with 300 and 600 oxygen molecules, respectively.

Figure 3-5. Initial configurations of ANPs: (a) with 300 oxygen molecules; (b) with 600 oxygen molecules

![Image](image1)

Figure 3-6. Number of oxygen atoms consumed and decrease in potential energy as a function of time at 300 K
The amount of oxygen consumption and decrease in the potential energy as a function of time were evaluated as shown in Figure 3-6. The potential energy of the system decreased drastically during the early stage (t < 4 ps) in which 65% of the oxygen molecules were consumed, confirming that the oxidation process is a highly exothermic reaction. Figure 3-7 and Figure 3-8 show cross sections of the system configurations and the temperature distributions, respectively.

Figure 3-7. Snapshots of the cross sections of system configurations of the ANPs at 300 K

Figure 3-8. Snapshots of the cross sections of temperature distributions of the ANPs at 300 K
Due to the highly exothermic reaction during the early stage, a couple of hot spots emerge \((T > 1000 \, \text{K})\), and a high temperature region \((T > 500 \, \text{K})\) existed near the surface of the ANPs during very short period time \((t \leq 0.5 \, \text{ps})\). Such hot spots almost had disappeared at \(t > 4.0 \, \text{ps}\), due to interaction with the thermostat. In real systems, the size of ANPs is relatively small as compared to that of a combustion chamber, which usually maintains a fixed temperature under certain experimental conditions. Consequently, the heat energy generated by the oxidation can be rapidly transferred to the surrounding environment by means of conduction or convection so that the inhomogeneous temperature distribution of the ANPs will disappear; this can be achieved by the thermostat algorithm during the MD simulations. \textit{i.e.,} the ANPs can exchange the heat energy with a very large heat bath (as compared to the system) to describe the canonical ensemble, and thus the system temperature will gradually reach at a target temperature, depending on the temperature damping constant.

![Figure 3-9. Local temperature of the outer surface of the ANPs: (a) at 0.0 ps; (b) at 1.0 ps and system configurations: (c) at 0.0 ps; (d) at 1.0 ps](image)
Figure 3-9a-d show that such hot spots and high-temperature regions generate void spaces (i.e., melted surfaces) near the outer surface, which may result in the rapid oxidation in the early stage. This can be proved by the rate of the growth of the oxide layer at 300 K, as shown in Figure 3-10.

Figure 3-10. The oxide layer thickness as a function of time at 300 K in the case of the low pressure of the oxygen gas.

Figure 3-11. Changes in total energy, potential energy, temperature as a function of time in microcanonical ensemble (initial oxygen density of 0.01 g/cm³).
The thickness of the oxide layer was almost completely developed within 50.0 ps, after which it attained its limiting thickness. Thus, the growth of the oxide film can be accelerated extensively during the oxidation process where hot spots and/or high temperature areas exist. However, oxygen densities used in this study (0.13 and 0.26 g/cm$^3$) are relatively high, compared to standard conditions for temperature and pressure ($0.14 \times 10^{-3}$ g/cm$^3$), and the system temperature were controlled by the thermostat. To ensure that the void space can be also generated at a relatively low oxygen density and without the thermostat, ReaxFF-MD simulations with a microcanonical ensemble (constant number of atoms, constant volume, and constant total energy) were performed at low oxygen gas density (0.01 g/cm$^3$) and initial temperature of 300 K. As shown in Figure 3-11, the total energy is conserved in the microcanonical ensemble and the temperature of the system increases up to ~800 K as a result of decrease in the potential energy during the oxidation process.

![Figure 3-12](image)

Figure 3-12. Formation of the void space as a function of time in microcanonical ensemble; the yellow circles represent evolutions of the local void space and the aluminum atoms generating the local void space are exaggerated.
Figure 3-12 shows the formation of void space on the outer surface of ANPs in the microcanonical ensemble up to 5.0 ps. It was found that the void space can be created at relatively low oxygen pressure and low initial temperature because the overall temperature of the system rise due to decrease in the potential energy. Thus, it is certain that the void spaces play a major role in the formation of the oxide layer during the oxidation process.

To confirm the effects of the void space on accelerating the growth of the oxide layer, the present study evaluated reaction barriers for oxygen diffusion on the fcc-Al crystal with and without the void space by the ReaxFF-MD simulations. By using a bond-restraint technique that determines the ReaxFF reaction profile at low temperature, an oxygen atom was forced to diffuse from an initial tetrahedral site to the nearest tetrahedral site.

![Figure 3-13](image)

Figure 3-13. System configurations of fcc-Al crystal with a single oxygen atom located on an initial tetrahedral site: (a) without void spaces; (b) with void spaces: The black arrows indicate the direction of the oxygen diffusion paths, and the red dots represent the void spaces.

Figure 3-13a-b show the configurations of the fcc-Al crystal with a single oxygen atom located on the initial tetrahedral site with and without the void spaces, respectively. For the case without void spaces, an expanded fcc-Al crystal cell (32-Al atoms) was used, and for the case with void spaces, two Al atoms on the initial tetrahedral site of the fcc-Al crystal were removed. It should be noted that the Al system with the void space is 196.0 kcal/mol higher in energy than the void
space-free system according to the ReaxFF description, but this energy is supplied by the exothermic Al-oxidation reaction and as such does not influence the barriers for the oxygen diffusion. Figure 3-14a-b show the reaction barriers for oxygen diffusion without and with void spaces, respectively. When the void spaces existed, the reaction barrier was reduced significantly from 36.0 to 2.9 kcal/mol (92%), and the nature of the reaction also changed to an exothermic event (-42 kcal/mol), meaning that the void space definitely accelerated the oxygen diffusion during the initial oxidation.

Figure 3-14. Reaction barriers to oxygen diffusion: (a) without void spaces; (b) with void spaces
Given the above results and observations, the mechanism of the oxidation of ANPs can be explained by the following: (a) highly exothermic reactions occur during the early stage in which many oxygen molecules are consumed; (b) due to the highly exothermic event, the surface temperatures of the ANPs increase, and a couple of hot spots are generated; (c) the increased surface temperature and hot spots result in the formation of void spaces on the ANPs, and (d) the void spaces accelerate the growth of the oxide layer by reducing the reaction barrier for oxygen diffusion.

### 3.3.3 The effects of burning conditions on the oxidation of the ANPs

In this section, the effects of the pressure of the oxygen gas and the temperature of the system on the growth of the oxide layer are reported. The ReaxFF-MD simulations were performed with initial oxygen densities of 0.13 and 0.26 g/cm$^3$ and temperatures of 300, 500, and 900 K.

**Oxygen gas pressure dependence**

In a previous experimental study,$^{46}$ it was reported that there is a strong dependence of the pressure of the oxygen gas on the oxidation of the ANPs, so that the overall kinetics of the oxidation of ANPs can be manipulated by the pressure of the oxygen gas instead of the temperature of the system. To demonstrate the effect of the pressure of the oxygen gas on the oxidation of the ANPs in the computational approach, two different conditions for the pressure of the oxygen gas were employed, *i.e.*, low pressure (initial oxygen density of 0.13 g/cm$^3$) and high pressure (initial oxygen density of 0.26 g/cm$^3$). Figure 3-15 shows comparisons of the decrease in potential energy and the temperature of the system at low and at elevated oxygen pressure.
The overall surface temperature during the early stage ($t \leq 2.0$ ps) were enhanced by elevated oxygen pressure. As a results, it took 4.0 ps for the surface temperature to stabilize at low oxygen pressure, whereas it took 6.0 ps at elevated oxygen pressure; the time to reach equilibrium was extended 50% when the density of the oxygen gas was doubled, indicating that the high pressure provided more opportunities for void spaces to form on the outer surface.

![Figure 3-15. Comparisons of the decreases of potential energy and local temperature of the ANPs in the cases of low and high pressure of the oxygen gas](image)

![Figure 3-16. Comparison of the rate of the growth of the oxide layer in the cases of the low and high pressure of the oxygen gas](image)
These results can be explained by the fact that the potential energy decreased at a faster rate when the pressure of the oxygen gas increased because the possible number of oxygen molecules bound to the surface of the ANPs increased with oxygen gas pressure. Since void spaces reduce the reaction barrier for the diffusion of oxygen (see Section 3.3.2), the thickness of the oxide layer can be expected to increase as the pressure of the oxygen gas increases. Figure 3-16 compares the rate of the growth of the oxide layer for the cases of low and high pressures of the oxygen gas. As expected, the rate of the growth of the oxide layer increased with oxygen pressure, so that the final thicknesses of the oxide layer at t = 1.0 ns at low and high pressure of the oxygen gas were 0.68 and 1.08 nm, respectively. Therefore, the growth of the oxide layer indeed depends on the pressure of the oxygen gas and there exists a direct relationship between oxygen pressure and the opportunity to generate void spaces on the outer surfaces of the ANPs.

**System temperature dependence**

During the oxidation process of ANPs at 300K and low oxygen pressure, the local temperature of the ANPs stabilized at t > 4.0 ps (see Figure 3-8) because the rate of decrease in the potential energy was greatly reduced at t > 4.0 ps (see Figure 3-6). That is, the hot spots (T > 1000 K) and high temperature areas (T > 500K), which induce the oxygen diffusion on the outer surface of ANPs, only emerge at the early stage (t < 4 ps) and then the bulk temperature is equilibrated at the system temperature of 300 K (t = 80 ps in Figure 3-8). Thus, after the temperature get stabilized, it can be presumed that the bulk temperature plays a crucial role on the oxygen diffusion throughout the bulk of ANPs. To verify this, the ReaxFF-MD simulations were performed at 300, 500, and 900 K. In Figure 3-17a, 3-17b, and 3-17c, the final snapshots (t = 1.0 ns) of the cross sections of the ANPs are shown at 300 K, 500K, and 900 K, respectively. The main observation is that the oxide layer thickness increases while raising the system temperature.
from 300 to 900 K. The rate of the oxide layer growth at the initial stage ($t \sim 50.0$ ps) is enhanced by increasing the system temperature, as shown in Figure 3-18.

Figure 3-17. Final snapshots ($t = 1.0$ ns) of cross sections of the ANPs in the case of the low pressure of the oxygen gas: (a) 300 K; (b) 500 K; (c) 900 K

Figure 3-18. Rate of the growth of the oxide layer on the ANPs in the case of the low pressure of the oxygen gas at three different temperatures: (a) 300 K; (b) 500 K; (c) 900 K

After the initial stage, there is a great reduction in the oxide layer growth so that the oxide layer essentially reached a limiting thickness at 300 and 500 K. However, at 900 K, the oxide layer does not attain the limiting thickness; the oxide layer continues to increase in thickness for 1000 ps. These results indicate that the oxide layer growth can be controlled by the system temperature because the oxygen diffusion in the bulk of ANPs occurs continuously at high temperature ($T >$
500 K). Hence, it can be suggested that, at high temperature, the oxide layer growth is not interrupted by the limiting thickness because of the increase in the probability that additional void spaces will be generated throughout the bulk of the ANPs.

The oxide layer growth on the ANPs is manipulated by both the pressure of the oxygen gas and the temperature of the system; the high pressure of the oxygen gas has the effect of generating additional void spaces on the outer surfaces of the ANPs, whereas the high temperature of the system enhances the formation of additional void spaces throughout the bulk of the ANPs.

3.3.4 Oxidation states of aluminum oxide layers: metal, sub-oxide, oxide, and super oxide

In this section, a formal analysis of the oxidation states of the ANPs is presented to investigate the transition from metal particles to aluminum oxides during the oxidation process. For this analysis, the oxidation states of Al-atoms were defined in terms of metal, sub-oxide, oxide, and super-oxide, as shown in Figure 3-19.

![Figure 3-19. Examples of oxidation states of Al-atoms: (a) metal; (b) sub-oxide; (c) oxide; (d) super-oxide. The oxidation states were defined by counting the number of Al- and O-atoms on a reference Al atom. The reference Al atoms are displayed by black circles.](image)
A percentage of Al- and O-atoms connected to reference Al-atoms was measured, and the reference Al-atoms were classified as follows:

(a) metal: the reference Al-atom is 100% surrounded by Al-atoms

(b) sub-oxide: the reference Al-atom is 60-90% surrounded by Al-atoms

(c) oxide: the reference Al-atom is 40-60% surrounded by Al-atoms

(d) Super-oxide: the reference Al-atom contains a peroxide group

These oxidation states were checked against the crystal structure of aluminum oxide (Al\textsubscript{2}O\textsubscript{3}); the thermodynamically most stable bulk structure of Al\textsubscript{2}O\textsubscript{3} is known to be a corundum form,\textsuperscript{67} and the aluminum atom in the corundum phase is about 40% surrounded by neighboring Al-atoms. Then, each oxidation state of the reference Al-atoms is counted between a radial distance, r and r + dr from the center of the ANPs. However, the surface area of the ANPs at r is proportional to a square of the radial distance, \textit{i.e.}, the longer the radial distance, the larger the surface area. To cancel out this effect, the number of each oxidation state of Al-atoms between r and r + dr was normalized by the number density multiplied by the volume of the spherical shell, similar to the concept of the radial distribution function.\textsuperscript{68} The normalized number of oxidation states, N(r), and the normalized radius of the ANPs, r\textsuperscript{*}, are defined as:

\begin{equation}
N(r) = \frac{n}{\rho 4\pi r^2 dr}
\end{equation}

\begin{equation}
r\textsuperscript{*} = \frac{r}{R}
\end{equation}

where n is the number of each oxidation state, \(\rho\) is the number density, and R is the radius of the ANPs. By using N(r), the transition from the metal state to the super-oxide state was evaluated with respect to both the temperature of the system and the pressure of the oxygen gas. Figure 3-20a-b show the transitions of the oxygen states with respect to the normalized radius of the ANPs in the case of the low pressure of the oxygen gas at 300 K and 900 K, respectively. At low temperature (T = 300 K), it was found that the oxide layer was developed mainly by the
transition from the metal (black curves) to sub-oxides (green curves), but no further significant transition can be found after 100 ps; the oxide layer has attained the limiting thickness. At high temperature ($T = 900$ K), the oxide layer also is developed mostly by the transition from the metal to sub-oxides, but such transition is expanded to the center of the ANPs so that the proportion of metals decreased greatly; as already observed, the oxide layer is not obstructed by the limiting thickness at high temperature. Thus, the oxide layer growth is affected mainly by the transition from metals to sub-oxides in case of the low pressure of the oxygen gas. In Figure 3-21(a), the transitions of the oxidation states are shown for the case of the high pressure of the oxygen gas at 300 K. Unlike the low pressure of the oxygen gas at which the oxide layer is primarily developed by the transition from metal to sub-oxide, the oxide layer is formed by increasing the portions of both sub-oxides and oxides (red curves). That is, the proportion of the sub-oxide at the high pressure of the oxygen gas is expanded to a deeper region of the ANPs than at the low pressure of the oxygen gas, and the transition from sub-oxides to oxides also increases. As mentioned earlier, at the elevate pressure of oxygen gas, there exists more opportunity to generate additional void spaces on the outer surface, and thus more oxygen atoms can diffuse to the bulk of ANPs so that both the transition from metal to sub-oxide, and from sub-oxide to oxide can be promoted. Subsequently, the oxide layer gets thicker and denser in the case of the high pressure of the oxygen gas; the amount of sub-oxide, oxide, and super-oxide is higher at the high pressure than at the low pressure of oxygen gas (see Figure 3-20a and Figure 3-21a). Figure 3-21b shows that this trend is more obvious at high temperature. At 900 K, the ANPs already are fully oxidized during the early stage ($t = 100$ ps); no metal components can be found through the bulk of the particle. Then, the transition from sub-oxides to oxides increases and the ANPs change to the amorphous aluminum oxide-nanoparticles.

Hence, it can be concluded that the temperature of the system affects mostly the oxide layer thickness, whereas the pressure of the oxygen gas affects the density of the oxide layer as
well the oxide layer thickness. Thus, the high enthalpy of combustion from the oxidation of the ANPs can be obtained by the combined effects of the high pressure of the oxygen gas and temperature of the system because these conditions effectively result in not only a thick but also a dense oxide layer.

![Figure 3-20. Oxidation states of the oxide layer in the case of the low pressure of the oxygen gas: (a) 300 K; (b) 900 K](image)
Figure 3-21. Oxidation states of the oxide layer in the case of the high pressure of the oxygen gas: (a) 300 K; (b) 900 K
3.4 Chapter Summary

In this chapter, the mechanism of the oxidation of ANPs with respect to the temperature of the system and the pressure of the oxygen gas were investigated theoretically, taking into account the oxide layer growth and the transition of the oxidation states. Major findings from Chapter 3 are as follows:

- The current ReaxFF description for aluminum/oxygen interactions qualitatively predicts the oxidation kinetics of the aluminum slab as a function of the temperature of the system; At low temperature (T ≤ 573 K), the oxide layer reaches the limiting thickness, whereas at high temperature (T ≥ 673 K), the oxide layer is not obstructed by the limiting thickness, which agrees with experimental studies.

- The mechanism of oxidation of the ANPs can be explained by the following: first, the highly exothermic reaction caused by the adsorption of the oxygen molecules results in the formation of the high temperature and hot-spot regions on the surfaces of the ANPs. Second, void space is created by the high temperature and/or the hot-spot regions. Last, the reaction barrier for oxygen diffusion can be reduced greatly by the void space, so the growth of the oxide layer increases.

- In terms of the oxide layer thickness, the rate of the oxide layer growth was enhanced by increasing the pressure of the oxygen gas and the temperature of the system; the high pressure of the oxygen gas increases the possible number of void spaces at the outer surfaces of the ANPs, whereas the high temperature increases the possible number of void spaces throughout the bulk of the ANPs.

- In terms of the oxidation states of the ANPs, the density of the oxide layer is affected by the combined effects of the system temperature and oxygen gas pressure; the transition from metal to sub-oxides is primarily expanded to the center of the ANPs by the
temperature of the system, while the transition from sub-oxides to oxides is mainly enhanced by the pressure of the oxygen gas, respectively.
Chapter 4

Growth kinetics of aluminum oxide layers on surface-modified aluminum nanoparticles

Chapter 4 is based on ref.69 authored by Sungwook Hong and Adri C.T. van Duin;
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4.1 Introduction

In previous Chapter 3, the mechanism of the oxidation process of bare aluminum nanoparticles (ANPs) was examined as a function of temperature and oxygen pressure. Unfortunately, the high reactivity of the ANPs, which is caused mainly by the increased surface-to-volume ratio, also produces a significant problem. The problem is that an excessive oxide layer on the surface of the bare ANPs is generated even at low temperatures (i.e., prior to the combustion process). This oxide layer decreases the energy release per unit mass because it basically is a worthless weight. An oxide layer that is only 4 nm thick constitutes about 50% of the total mass of a 40nm diameter ANPs.11-13 To overcome this challenge, a carbon coating on the bare ANPs was proposed because it offers several advantages, (a) the carbon coating basically is less reactive at low temperatures, but its reactivity remains at elevated temperatures, (b) carbon-coated ANPs have a hydrophobic nature, thus repelling potential oxidants like water, and (c) the carbon coating serves as an additional source of fuel.70-71 Consequently, many researchers have focused on effects of an organic coating on the oxidation of the ANPs. For example, Jouet et al.14 conducted experiments to determine the extent of surface passivation of bare ANPs using
perfluoroalkyl carboxylic acids in wet conditions, and they reported that the energy release of ANPs can be enhanced by the proper selection of the carboxylic acid used in the process. Sossi et al.\textsuperscript{12} also examined the protection of ANPs passivated by non-inert coatings (e.g., stearic acid, oleic acid, and fluoropolymer solutions), but they concluded that such organic layers can be oxidized even at low temperatures, thereby forming an internal oxide layer inside the organic layer. The most relevant work was conducted by Park et al.\textsuperscript{70}, who investigated the characteristics of a carbon coating on ANPs using a laser-induced plasma. In their work, the carbon coating was generated by adding ethylene downstream of the plasma, and the carbon-coated ANPs were thermally oxidized at temperatures ranging from 573 to 1173 K. They found that, after the plasma coating, the previously bare ANPs had been covered by carbon and hydrogen, and they emphasized that the carbon-coated ANPs resisted oxidation up to a temperature of 1073 K. Subsequently, a similar study was conducted by Guo et al.\textsuperscript{72} who performed the carbon coating of ANPs using complex laser-induction heating with a precursor of methane. They demonstrated that the carbon-coated ANPs had a much higher reactivity than the Al\textsubscript{2}O\textsubscript{3}-passivated ANPs at elevated temperature and that the energy release of the carbon-coated ANPs could be enhanced by the additional oxidation of the carbon components. Thus, based on the previous studies, it can be expected that coating ANPs with carbon can enhance the energy efficiency, making them suitable for use in solid-fuel rockets.

However, relatively little work has been done to elucidate the process by which hydrocarbon precursors form the carbon coating layer on the bare ANPs. In addition, the role of carbon coating on the oxidation kinetics of ANPs has not yet been fully understood. For these reasons, the present study proposes to develop a ReaxFF\textsuperscript{20} reactive force field for Al/C interactions, and then, to investigate the kinetics associated with the growth of the carbon coating layer on the bare ANPs, and subsequent oxidation of the carbon-coated ANPs. As such, the aim of this work is to evaluate the agreement between the ReaxFF method and quantum mechanics
(QM) and experimental results, and subsequently use this method to analysis of the effects of the carbon coating layer on the oxidation kinetics of the ANPs.

4.2 Computational details

4.2.1 QM method

In order to expand the ReaxFF description to the Al/C/H/O system, QM calculations were conducted for both periodic and non-periodic systems. In case of the periodic system, the commercial density functional theory (DFT) tool of Vienna ab initio Simulation Package (VASP)\textsuperscript{73} was used. For Al, C, and H atoms, the PAW potentials\textsuperscript{74-75} generated with the generalized gradient approximation (GGA-PBE)\textsuperscript{76} were used, and the maximum cutoff value of 400 eV for the plane wave basis set was chosen with an acceptable energy convergence (e.g. C atom's adsorption energies on the Al (111) surface with the maximum cutoff values of 400 eV and 520 eV were 170.16 and 169.94 kcal/mol, respectively; within 0.15\% difference). A rhombohedral crystalline structure (space group \textit{R-3m}) was chosen for a bulk of aluminum carbide (Al\textsubscript{4}C\textsubscript{3}) with the lattice parameter of \(a = 3.355 \text{ Å}\) and \(c = 25.122 \text{ Å}\). A slab model used in this study was an Al (111) surface; six layers of the Al (111) slab (4.96 Å × 5.76 Å × 28.08 Å) in an orthogonal simulation box were used, including a vacuum layer of 20 Å and the lowermost three layers were fixed with good accuracy (within 0.20\% error). \textit{i.e.}, C atom's adsorption energies on the Al (111) slab with the lowermost three, four, and five layers fixed were found to be 170.16, 170.28, and 170.04 kcal/mol, respectively. For numerical meshes, an \(8 \times 8 \times 8\) Gamma \(k\)-point grid was used for bulk calculations of the aluminum carbide, and a \(5 \times 5 \times 1\) Monkhorst-Pack\textsuperscript{77} \(k\)-point grid was used for the adsorption/decomposition of hydrocarbon radicals and hydrocarbon species (ethane, ethylene, and acetylene) bound to the Al (111) surface.
Reaction barriers for the decomposition of hydrocarbons and C₂ dissociation on the Al (111) surface were determined using the nudged elastic band (NEB) method with the Limited-memory Broyden-Fletcher-Goldfarb-Shanno (L-BFGS) optimizer. Three intermediate images were considered for each of the NEB calculations. In case of the non-periodic clusters that contained Al/C/H/O atoms, the rapid ab initio electronic structure package of Jaguar 8.3 was used with the B3LYP functional and 6-311G** basis set. To obtain the QM-based structures in the training set, full geometry optimizations were performed for all non-periodic clusters. In addition, relaxed geometry scans with certain bonds and angles were performed to attain full bond dissociation curves and angle distortion energy for Al/C interactions.

4.2.2 Force field training

The present study began to develop and extend the ReaxFF parameters for Al/C/H/O by incorporating the most recent Al/O description available in Hong and van Duin and re-training the Al/H description. That is, ReaxFF parameters for Al/C interactions were exclusively optimized, and subsequently Al/H parameters were re-optimized to describe complex Al/C/H/O systems. Further information of history of ReaxFF development for Al/O and Al/H parameters can be available in the recent ReaxFF review paper. Please note that during the force field training in this study, the Al/O parameters were kept unchanged and the Al-H parameters were re-trained by including the previous Al/H training set in our current training set. These strategies enable us to maintain the level of the previous agreement between the DFT and ReaxFF data for the Al/H/O-related interactions. For QM data in the training set, QM calculations were included in the following: (a) equations of state (EOS) for the aluminum carbide; (b) adsorption and decomposition energies of hydrocarbons on the Al(111) surface; (c) bond dissociation/angle distortion energies for Al/C/H/O clusters. While training the ReaxFF force field, all initial
structures derived by the QM calculations were optimized fully with certain bond/angle restraints and/or fixed layers. Thus, 144 data points were included in the ReaxFF training sets, and 49 ReaxFF parameters were trained primarily to describe the Al/C interactions.

4.2.3 Simulation details

Molecular dynamics (MD) simulations with the developed ReaxFF reactive force field were performed using a canonical ensemble (i.e., a constant number of atoms, a constant volume, and a constant temperature) to study the temperature-controlled, carbon coating process and the oxidation of the carbon-coated ANPs. For these procedures, the Berendsen thermostat with a damping constant of 100 fs were employed, and the ADF code with 4-8 processors was used. Because the previous ReaxFF study indicated that the time step should be lower than one order of the highest frequency of the simulated system (normally, t ~ 0.5 – 1.0 fs), and because the MD simulations were performed under a relatively high temperature range (2500 – 3000 K), this study chose to use the time step of 0.1 fs, which enabled us to correctly capture reaction events for the carbon coating/oxidation processes up to 3000 K. The bare ANPs consisting of 864 Al atoms were obtained from the previous ReaxFF study, as reported in Chapter 3. All of the system configurations and snapshots in this study were prepared using Molden and VMD software.

4.3 Results and discussion

4.3.1 Force field development

In order for the ReaxFF description to simulate complex Al/C/H/O systems, ReaxFF parameters were primarily chosen to optimize as follows:
a. Al-C bond parameters

b. Al-C off diagonal parameters

c. A/C angle parameters: C-Al-C; Al-C-Al; H-C-Al; C-Al-O; C-C-Al; C-Al-Al

After optimizing the Al/C parameters and subsequently combining them with the Al/H and Al/O parameters, it was found that geometries of Al/C/H/O clusters derived by the ReaxFF (e.g., C-H or Al-C equilibrium bond distances) were not consistent with the DFT calculations, and thus, additional Al/H parameters were decided to re-train as follows:

a. Al-H bond parameters

b. Al-H off diagonal parameters


As such, this section reports the extent of QM calculations for the force field training set and the ReaxFF fits to the QM calculations.

**EOS for Al₄C₃**

The most stable crystal structure for aluminum carbide is known to be a rhombohedral crystalline structure.⁸² To predict the structural behaviors of aluminum carbide, the total energy of the aluminum carbide for the expansion and compression ranges were calculated, and the bulk modulus and equilibrium lattice constants were obtained by fitting against the Birch-Murnaghan EOS.⁸³ Figure 4-1 shows the ReaxFF parameters' fit to the EOS for the rhombohedral aluminum carbide. The ReaxFF appropriately reproduces the EOS for the rhombohedral aluminum carbide. In addition, as listed in Table 4-1, the ReaxFF correctly predicted the characteristics of the crystal structure (the bulk modulus and the equilibrium lattice constants), consistent with the previous experimental⁸² and theoretical⁸⁴ studies.
Table 4-1 Comparison of bulk properties (lattice parameters, c/a ratio, and bulk modulus) of the rhombohedral aluminum carbide in the experimental and theoretical approaches

<table>
<thead>
<tr>
<th>Method</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
<th>Bulk modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expt.(^{42})</td>
<td>3.339</td>
<td>25.006</td>
<td>7.489</td>
<td>130</td>
</tr>
<tr>
<td>DFT (GGA-PW11)(^{41})</td>
<td>3.281</td>
<td>24.547</td>
<td>7.482</td>
<td>170</td>
</tr>
<tr>
<td>DFT (GGA-PBE) – this study</td>
<td>3.355</td>
<td>25.122</td>
<td>7.488</td>
<td>116</td>
</tr>
<tr>
<td>ReaxFF – this study</td>
<td>3.359</td>
<td>25.153</td>
<td>7.488</td>
<td>140</td>
</tr>
</tbody>
</table>

**Adsorption and decomposition of hydrocarbon radicals on Al(111) surface**

To simulate the carbon coating process on the ANPs using hydrocarbon precursors, it is essential that the ReaxFF has the capability of capturing chemical reactions between the
hydrocarbon radicals and aluminum surfaces. For this reason, the ReaxFF parameters were trained against DFT calculations of the adsorption and decomposition of hydrocarbon radicals on the Al(111) surface. In the case of the adsorption of hydrocarbon radicals on the Al(111) surface, three hydrocarbon radicals (CH, CH₂, and CH₃) and single C atom were considered, and the adsorption energies were calculated using Equation 10.

\[
E_{\text{adsorption}} = E_{\text{Al slab}} + E_{\text{isolated adsorbate}} - E_{\text{Al slab/adsorbate}},
\]

(10)

where \(E_{\text{Al slab}}\), \(E_{\text{isolated adsorbate}}\), and \(E_{\text{Al slab/adsorbate}}\) are the energy of a clean Al(111) surface, the energy of isolated hydrocarbon radicals, and the energy of the Al(111) surface with adsorbed hydrocarbon radicals or C atom, respectively.

Based on the DFT calculations, it was found that energetically favorable sites for the CH, CH₂, and CH₃ radicals and the C atom on the Al(111) surface are a hollow, bridge, on-top, and hollow site, respectively. Figure 4-2 shows the results of the ReaxFF optimization for the adsorption energies of the CH₃, CH₂, and CH radicals and the C atom on the Al(111) surface. The ReaxFF calculations were in good agreement with the DFT calculations (within a maximum of 13.8% difference), and the ReaxFF-optimized structures correctly reproduce the DFT-derived binding sites for the C, CH, CH₂, and CH₃ species. In addition, as shown in Figure 4-3a-c, the ReaxFF parameters were trained to reproduce qualitatively the reaction barriers and energies for the decomposition of the hydrocarbon radicals on the Al(111) surface. That is, although the reaction barriers of the hydrocarbon radicals' decomposition, described by the ReaxFF are a relatively low when compared to the DFT data, the ReaxFF has the ability to quantitatively describe reaction kinetics of the hydrocarbon radicals' decomposition on the Al surfaces.
Figure 4-2. Comparison of adsorption energies of CH$_3$, CH$_2$, CH, and C on Al (111) in the DFT and ReaxFF results (sky blue: Al atoms, brown: C atoms, and white: H atoms)

Figure 4-3. Reaction energies and barriers for (a) CH$_3$, (b) CH$_2$, and (c) CH radicals decomposition on Al (111) derived by the DFT and ReaxFF calculations
**Bond dissociation and angle distortion energies for Al/C/H/O clusters**

DFT calculations of the bond dissociation and angle distortion energies for Al/C/H/O clusters were performed, and the ReaxFF parameters were fitted against the results of these calculations. Figure 4-4 and Figure 4-5a-d show the ReaxFF parameters' fits to the bond dissociation and angle distortion energies.

Figure 4-4. ReaxFF parameters' fit to the Al-C full bond dissociation curve obtained by the DFT calculations.

Figure 4-5. ReaxFF parameters' fit: (a) to Al-C-Al; (b) to C-Al-C; (c) to H-C-Al; (d) to C-Al-O angle distortion energies, derived by the DFT calculations.
Because the ReaxFF description basically does not contain the concept of multiplicity (e.g., single or triplet state), the ReaxFF parameters fit against the lowest energy between the single and triplet states obtained by the DFT calculations in case of the Al-C bond energy. The results of the ReaxFF fits indicated that the ReaxFF description was able to reproduce the full dissociation energy curve for the Al-C bond, and the angle distortion energies for the Al/C/H/O clusters.

4.3.2 Force field validation

To validate the developed ReaxFF parameters for Ge/Al/C/H/O interactions, the present work conducted additional ReaxFF calculations and compared the results with additional DFT calculations as follows: (a) hydrocarbons binding to the Al(111) surface; (b) C₂ dissociation on the Al(111) surface. The aim of this validation is to check if the ReaxFF parameters developed in this study can qualitatively describe chemical reactions which were not included in our training set.

Binding of hydrocarbons to the Al(111) surface

Because the ReaxFF description was developed primarily to investigate the process of coating the bare ANPs with carbon by using hydrocarbon precursors, it was necessary for the ReaxFF description to predict correctly the behavior of the hydrocarbons in binding to the Al surface. Figure 4-6 compares the binding energies of three hydrocarbon species (ethane, ethylene, and acetylene) on the bridge site of the Al(111) surface in the DFT and ReaxFF calculations; ethane, ethylene, and acetylene molecules are initially placed at on-top, top-fcc, and fcc-hcp sites, respectively. Although the ReaxFF calculations were somewhat overestimated or underestimated when compared to the DFT calculations (e.g. the maximum difference between the DFT and
ReaxFF calculations in the binding energy is found to be \( \sim 9 \text{ kcal/mol} \) in case of ethylene species), it was observed that the overall ReaxFF results agreed qualitatively with the DFT results. That is, the hydrocarbon species for the maximum binding energy was found to be acetylene, followed by ethylene and ethane, based on both the ReaxFF and DFT calculations. These results indicate that the ReaxFF description was applicable to the chemistry associated with the interactions of three different hydrocarbons with the Al surface.

Figure 4-6. DFT versus ReaxFF calculations for ethane, ethylene, and acetylene binding on the Al (111) surface.

\( \text{C}_2 \text{ dissociation on the Al (111) surface} \)

To elucidate the stability of a C-C bond on the Al surface during the carbon coating process and to verify that the ReaxFF treats this characteristic correctly, a reaction path for the \( \text{C}_2 \) dissociation on the Al(111) surface was evaluated using both the ReaxFF-NEB and DFT-NEB methods; the \( \text{C}_2 \) molecule was placed on the bridge site of the Al (111) at the initial configuration;
at the final configuration, the C-C bond breaks and then two C atoms are diffused on the three-fold hollow site and the next tetrahedral site of the Al(111) surface, respectively.

Figure 4-7. Reaction path for breaking a C-C bond on the Al(111) surface calculated by means of the ReaxFF-NEB and DFT-NEB methods: The silver color indicates Al atoms and the green color indicates C atoms.

Figure 4-7 shows the reaction path and profile for the C₂ dissociation. On the one hand, it can be expected that, because the ReaxFF-NEB calculations underestimate energies of image 2 and 3, obtained by the DFT-NEB, ReaxFF-MD simulations would derive intermediate structures (image 2 and 3) with a relatively low temperature input (i.e., a low average kinetic energy of the system). On the other hand, based on the DFT-NEB scheme, it was found that this reaction has a high reaction barrier (97.6 kcal/mol) and high endothermicity (80.7 kcal/mol). Obviously, the ReaxFF-NEB results reproduced those DFT values quantitatively, i.e., a reaction barrier of 99.8 kcal/mol and a reaction energy of 95.9 kcal/mol. Thus, the analysis of the results of both ReaxFF-NEB and DFT-NEB confirmed that breaking the C-C bonds on the Al(111) surface is energetically unfavorable.
4.3.3 MD simulations of carbon coatings and subsequent oxidation of ANPs

This section reports investigation of the carbon coating process on the bare ANPs using hydrocarbon precursors, and subsequent oxidation process on the carbon-coated ANPs, described by the ReaxFF reactive force field method.

**Carbon coatings on the bare ANPs using ethylene precursors**

To ensure that the ReaxFF description has the ability to access the full dynamics of carbon coating on the bare ANPs with hydrocarbon precursors, ReaxFF-MD simulations of the chemisorption of ethylene molecules on the bare ANPs were performed, which was conducted previously in an experimental study. The experimental results indicated that the carbon coating was achieved by means of a laser-induced plasma using the ethylene precursors, thus allowing them to be thermally cracked and heterogeneously deposited on the bare ANPs. To describe such a nucleation using the ReaxFF-MD simulations, 864 Al atoms of the bare ANPs were placed in the middle of the orthogonal simulation box (45 × 45 × 45 Å), and 350 ethylene molecules were distributed randomly, as shown in Figure 4-8a. Then, two different temperature zones were used for a single cycle, i.e., (1) the ANPs at 300 K and (2) the ethylene molecules at 2500 K for 15 ps, and, subsequently, the ethylene precursors were cooled down to 300 K within 8.5 ps. By doing this, the deposition and the decomposition of the ethylene molecules can be accelerated on the surface of the bare ANPs, while the cores of the ANPs remained in the solid state. In addition, because all of the C and H atoms in the system were cooled down to 300 K at the end of each cycle, their diffusion into the ANPs' sublayers could be prevented, which is caused by elevated temperature. All of the gas phase molecules were removed after the single cycle, and, then, new 350 ethylene molecules were redistributed for the next cycle.
Figure 4-8. (a) Initial configuration of 350 ethylene molecules and 864 Al atoms of the ANPs. (b) Changes in the adsorption ratio as a function of the coating cycles. (c) Evolution of the carbon coating layer on the ANPs using ethylene precursors up to six cycles, derived by MD simulations. (d) SEM images of uncoated and carbon-coated ANPs. Note that the carbon-coated ANPs was experimentally prepared by the dry coating with carbon black (Reprinted from ref 85 with permission from Elsevier).
To perform a quantitative analysis of the extent to which the ANPs' surfaces were saturated with respect to each cycle, an adsorption ratio of the ethylene precursors was defined as Ethylene(ads)/Ethylene(g). Figure 4-8b shows that the adsorption ratio increased up to two cycles, after which it decreased gradually for the additional cycles. During our simulations, it was found that the adsorption ratio with six cycles decreased to ~ 5%, indicating that the ANPs' surfaces almost were saturated by the C and H elements. As such, this study considered the structure with three cycles to be partially carbon-coated ANPs, and considered six cycles to be almost fully carbon-coated ANPs. Figure 4-8c shows the evolution of the carbon coating layer on the bare ANPs up to six cycles. It is apparent that the portion of C and H coverage was increased by proceeding with the cycles. This result was consistent with the experimental result, confirming that a thin layer of both C and H elements had been deposited on the ANPs. Consequently, it can be expected that surface roughness on the carbon-coated ANPs increases because the carbon elements were unevenly deposited, thus providing a number of local protrusions on the outer surface of the ANPs (see the high magnification images in Figure 4-8c). This was also confirmed by the previous experimental study, reporting that nano-scale roughness of the carbon-coated ANPs, prepared by dry particle coating with carbon black, increased as compared to the untreated ANPs based on the analysis of scanning electron microscope (SEM) images from Jallo et al. (Figure 4-8d). Thus, it is noteworthy that the surface morphology of the carbon-coated ANPs, obtained by the ReaxFF description, qualitatively agreed with the experimental data.

Additionally, Figure 4-9a and b show the cross section of the carbon-coated ANPs with six cycles (ReaxFF) and the transmission electron microscopy (TEM) image of the ANPs with the laser-induced plasma coating (experiments), respectively. Both the theoretical and experimental samples demonstrate that the carbon elements primarily generated a thin layer on the ANPs’ surfaces, while the metallic component of the core of the carbon-coated ANPs remained unchanged; the components of the coating layer (C and H atoms) obtained by the ReaxFF-MD
simulations were consistent with the experimental study,\textsuperscript{70} reporting that after the laser-induced plasma treatment, the ANPs were coated with a shell structure of C and H atoms. The experimental study also found that the elemental ratio of C/Al on the carbon-coated ANPs increased as the diameters of the particles decreased (Figure 4-9c).

Figure 4-9. (a) A cross-section of the carbon-coated ANPs with six cycles observed by the ReaxFF-MD results (green: C atoms; silver: Al atoms; white-transparent: H atoms). (b) TEM image of carbon-coated ANP (Reprinted from ref\textsuperscript{70} with permission from Springer). (c) Elemental ratio of C/Al on the carbon-coated ANPs from the experimental data,\textsuperscript{70} the power-law fit to the representative experimental data points. Please note that the power-law curve for

Because the particle diameter (~ 4 nm) in this study was not in the experimental range, the present study compared the elemental ratio of C/Al obtained by the ReaxFF results with a power-law fit to the representative experimental data points. Please note that the power-law curve for
fitting the experimental data was chosen to use because a R-Square value of the power-law curve (0.70) is higher than that of a linear curve (0.65) and an exponential curve (0.60), indicating that 5-7% more variations can be explained by the power-law curve when compared to the linear or exponential curves. This analysis suggests that the C/Al ratio of the carbon-coated ANPs with six cycles (the ReaxFF results) is qualitatively consistent with the experimental results.

Given the results of the ReaxFF-MD simulations and their comparison with the experimental literature above, it can be suggested that the developed ReaxFF description has the capability of studying carbon coating on ANPs using hydrocarbon precursors.

**Formation process of the carbon coating layer on the bare ANPs**

This section investigates the surface chemistry of hydrocarbon deposition on the bare ANPs in an atomistic-scale view point. For this analysis, the first cycle of the carbon coating using the ethylene precursor was considered. Figure 4-10 shows the ethylene chemisorption/decomposition on the bare ANPs during the carbon coating, as derived by the ReaxFF-MD simulations. A detailed formation process for the ethylene deposition is as follows: (1) the bare ANPs are surrounded by ethylene molecules at 0.14 ps; (2) the ethylene molecules chemisorb non-dissociatively on the Al binding site available at 0.28 ps; (3) hydrogen transfer occurs from the ethylene molecule to the neighboring Al binding site at 0.60 ps; (4) residual H atoms on the ethylene molecules transfer to the nearest Al binding sites, and, finally, the C₂ is deposited on the surface of the ANPs at 1.40 ps. It should be noted that breaking C-C bonds was not observed during the ethylene deposition up to six cycles. This formation process can be attributed to the fact that the all of H diffusion from hydrocarbon radicals to the neighboring Al binding sites has a low reaction barrier when compared to the C₂ dissociation on the Al surface (see reaction barriers in Figure 4-3 and Figure 4-7). Also, the endothermicity of C₂ dissociation
on the Al surface, as confirmed by the ReaxFF and DFT calculations in Figure 4-7, is higher than that of the hydrocarbon radicals decomposition on the Al surface. As such, one can be expected that at given temperatures, hydrocarbon species can initially be dissociated on the Al surface by transferring H atoms to Al binding sites and subsequently, breaking C-C atoms can be feasible at further elevated temperatures.

In summary, based on reaction kinetics from the Reax-MD simulations (ethylene precursors at 2500 K and ANPs at 300 K), it was observed that the hydrocarbon precursors are deposited
mostly via the transfer of only H atoms, thus forming the protective layer on the surface of the bare ANPs without the dissociation of C\(_2\).

![Graph of elemental ratio of C/Al on the carbon-coated ANPs using ethane, ethylene, and acetylene precursors.](image)

Figure 4-11. (a) ReaxFF-MD results of the elemental ratio of C/Al on the carbon-coated ANPs using ethane, ethylene, and acetylene precursors. (b) Cross sections of the carbon-coated ANPs with six cycles. The thickness of the carbon coating layer depends on the hydrocarbon precursors.

In addition to the ethylene precursor, two additional hydrocarbon species were used: ethane and acetylene, to study hydrocarbon precursors' dependence of the growth of carbon coating layer on the bare ANPs. In Figure 4-11a, the effects of the hydrocarbon precursors on the elemental ratio of C/Al are shown. Up to six cycles, the highest elemental ratio of C/Al was found to be the acetylene precursor, followed by the ethylene precursor and then the ethane precursor. As a result, the carbon coating layer using the acetylene precursor was thicker than those of the other precursors; a relatively small amount of the hydrocarbon species was chemisorbed in the
case of the ethane precursor (Figure 4-11b). These results can be explained by the fact that the acetylene precursor preferably chemisorbs on the Al surface, as compared to the ethylene and ethane precursors, since it has the highest binding energy among these three species (see Figure 4-6). Thus, it can be suggested that the growth of the carbon coating layer on the ANPs can be controlled by using different hydrocarbon precursors.

**Oxidation of the carbon-coated ANPs at low and high temperatures**

Basically it can be expected that the carbon coated ANPs can resist oxidation at low temperatures, but they can be susceptible to oxidation at high temperatures because carbon is less reactive only at low temperatures. To demonstrate whether the carbon coating layer effectively serves as a protective layer, ReaxFF-MD simulations of the oxidation of the carbon-coated ANPs were performed at 300 and 3000 K. After the bare ANPs had undergone six cycles of the carbon coating treatment (with the ethylene precursor), they were considered to be carbon-coated ANPs, and both the carbon-coated ANPs and 600 O₂ gas molecules were placed in the orthogonal simulation box (60 × 60 × 60 Å). Figure 4-12a shows the initial configuration of the carbon-coated ANPs and the 600 O₂ molecules. Snapshots of MD simulations of the oxidation of the carbon-coated ANPs with respect to both time (50 and 150 ps) and temperatures (300 and 3000 K) are shown in Figure 4-12b. It should be noted that the time scale used in this study (150 ps) is relatively short, compared to experimental conditions, because of a limited time step in ReaxFF-MD simulations (~ fs) and computational source. To overcome such limitations, this study used higher oxygen density (0.15 g/cm³) than a standard condition (0.14 × 10⁻³ g/cm³) to accelerate the oxidation kinetics at a given time frame, also chosen by our previous study.³⁷ These snapshots indicate that, at 3000 K, a larger number of O₂ molecules were adsorbed on the carbon-coated ANPs than at 300 K; the adsorbed O₂ molecules readily dissociated at 3000 K, but,
at 300K, the majority of them maintained their peroxide states (see the high magnification images in Figure 4-12b).

Figure 4-12. (a) Initial configuration of 600 oxygen molecules and carbon coated ANPs. (b) Snapshots of the ReaxFF-MD simulations of the oxidation of the carbon-coated ANPs at 300 and 3000 K with respect to time.
This effect was also confirmed by analyzing the number of adsorbed O₂ molecules as a function of time, as shown in Figure 4-13. At the initial stage (up to 5 ps), the number of adsorbed O₂ molecules per time unit at 300 K, obtained by a linear curve fit (with a R-Square of 0.94) was found to be 19 molecules/ps while at 300 K, the value was 25 molecules/ps (obtained by a linear curve fit with a R-Square of 0.96); at 150 ps, the number of adsorbed O₂ at 3000 K was 46 % greater than at 300 K. Thus, the ReaxFF-MD results suggest that the O₂ physisorption and chemisorption on the carbon-coated ANPs can be controlled by the system temperature.

Figure 4-13. Number of adsorbed oxygen molecules during the oxidation of the carbon-coated ANPs at 300 and 3000 K

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>H₂O (g)</th>
<th>H₂ (g)</th>
<th>CO (g)</th>
<th>CO₂ (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3000</td>
<td>520</td>
<td>10</td>
<td>5</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 4-2 Analysis of the gas phase products resulting from the oxidation of the carbon-coated ANPs at 300 and 3000 K using the ReaxFF-MD simulations (150 ps)
To demonstrate how the coating layer protects against oxidation only at low temperature, as discussed above, the number of gas phase products in the system was monitored at 300 and 3000 K (150 ps). Table 4-2 shows that, at 150 ps, several gas phase products were identified at 3000 K, such as 520 products of H$_2$O, 10 products of H$_2$, 5 products of CO, and 3 products of CO$_2$, but no gas phase products were observed at 300 K. The analysis of gas phase products indicates that the components of the coating layer (C and H atoms) were removed at the elevated temperature due to their interactions with O$_2$ molecules, resulting in the products of H$_2$O, H$_2$, CO, and CO$_2$.

Consequently, the available portion of Al binding sites increases, allowing for more O$_2$ molecules to be adsorbed and dissociated at the surface of the carbon-coated ANPs. These results were consistent with the results of the experimental study$^{70}$ (in which it was reported that the oxidation rate of the carbon-coated ANPs increased at high temperature because the coating layer is stripped off), and, thus, the ReaxFF-MD results confirm that the carbon coating layer was capable of protecting against oxidation only at low temperature, and also suggest how the coating layer is removed at elevated temperatures in an atomistic-scale view point.

### 4.4. Chapter Summary

The effects of carbon coating on the oxidation of ANPs was investigated using the ReaxFF description for Al/C interactions, as developed in this study. The conclusions drawn from this study are as follows:

- The developed ReaxFF description for Al/C interactions correctly describes the EOS of aluminum carbide, the adsorption/decomposition of hydrocarbon radicals on the Al(111) surface, the full dissociation curve of the Al-C bond, and the angle distortion energies of the Al/C/H/O clusters.
• The ReaxFF description qualitatively reproduces the C\textsubscript{2} dissociation and hydrocarbon species (ethane, ethylene, and acetylene) binding energies on Al(111) surfaces, derived by the DFT calculations, indicating that the ReaxFF description is capable of describing reaction kinetics of systems, not included in our training set explicitly.

• The ReaxFF-MD simulations of the carbon coating process suggest that the growth of the coating layer depends on the hydrocarbon precursors, and the hydrocarbon precursors are deposited via H atoms transfer, but without breaking C-C bonds.

• The ReaxFF-MD results also confirm that, at elevated temperature, the oxidation rate of the carbon-coated ANPs was enhanced by removing the coating layer by forming H\textsubscript{2}O, H\textsubscript{2}, CO, CO\textsubscript{2}, thus providing an atomistic-scale insight into the role of carbon coating during the oxidation of ANPs. Therefore, the ReaxFF description opens the possibility to further investigate complex surface chemistry of surface-modified ANPs.
Chapter 5

Growth kinetics of aluminum oxide layers on Ge-based semiconductors


In addition, it should be noted that experimental works (i.e., Al\textsubscript{2}O\textsubscript{3} ALD on hydrogen-terminated and oxidized Ge surfaces), reported in Chapter 5, were exclusively carried out and analyzed by Dr. Engel-Herbert's research group in the Department of Materials Science and Engineering at The Pennsylvania State University. All the simulation work and analyses of results from the simulations, including those from the above reference and other sections in Chapter 5 were conducted by Sungwook Hong.

5.1 Introduction

In this chapter, growth kinetics of the aluminum oxide layers on Ge-based semiconductors were investigated for application to the next-generation ultrathin gate stacks. In recent years, the dimension of Si-based semiconductor devices has approached its physical limits as the scaling of transistors has decreased steadily.\textsuperscript{87-88} In an effort to replace Si, Ge has been
considered as a promising candidate for complementary metal oxide semiconductor (CMOS) technology because Ge-based CMOS devices have several advantages, such as higher carrier mobility, lower processing temperature, and lower operational voltage, over Si-based devices.\textsuperscript{87, 89-91} To make the Ge-based CMOS technology attractive in the semiconductor industry, it is necessary to manufacture high-\(\kappa\) (such as HfO\(_2\) and ZrO\(_2\))/Ge gate stacks,\textsuperscript{92} which possess both an ultrathin equivalent oxide thickness and low interface state density (\(D_{it}\)).\textsuperscript{15} Unfortunately, recent studies have pointed out that a direct deposition of high-\(\kappa\) materials on Ge substrates worsens electrical properties between the high-\(\kappa\)/Ge interfaces. That is, an amount of \(D_{it}\) increases due to the direct deposition of high-\(\kappa\) materials on the Ge substrate.\textsuperscript{93-94} In order to tackle such a problem, depositing an ultrathin GeO\(_2\) interfacial layer (IL) between the high-\(\kappa\) material and the Ge substrate has been suggested because the GeO\(_2\) IL is known to exhibit excellent \(D_{it}\) (\(\sim 10^{11}\) cm\(^{-2}\) eV\(^{-1}\)) at the GeO\(_2\)/Ge interface.\textsuperscript{15, 95} Although the GeO\(_2\) IL can be considered a promising option between the high-\(\kappa\) materials and the Ge substrate, the thermal instability of the GeO\(_2\)/Ge interface is a major challenge for this application when compared to SiO\(_2\)/Si interface. For example, Kita \textit{et al.}\textsuperscript{96} investigated the thermal characteristics of GeO\(_2\) film with annealing processes and explained that GeO desorption occurs at the GeO\(_2\)/Ge interface during the annealing, resulting in a serious worsening of the electrical characteristics of the GeO\(_2\)/Ge metal-insulator-semiconductor capacitor. They pointed out that the GeO desorption originates from the reaction between a GeO\(_2\) layer and a Ge substrate, but not the GeO\(_2\) bulk phase itself up to 973 K. A similar result was reported by Prabhakaran \textit{et al.},\textsuperscript{97} who examined a thermal decomposition pathway for an ultrathin oxide layer on Ge(100) slab and concluded that during the annealing, a surface transformation from GeO\(_2\) to GeO emerges up to 700 K as GeO\(_2\) layers reacts with Ge substrates, and the GeO species desorb at a higher temperature.

To overcome this challenge, additional passivation layers must be sought on the GeO\(_2\) IL, which allows us to enhance the thermal instability of the GeO\(_2\)/Ge interface. In that regard, the
Al₂O₃ layer was found to be suitable for an additional IL between the high-κ and the GeOₓ/Ge substrate because the Al₂O₃ layer has the ability to prevent undesired growths of GeOₓ at the GeO₂/Ge interface.¹⁵,¹⁸ For this reason, an atomic layer deposition (ALD) has been typically used to deposit the Al₂O₃ layers between the high-κ materials and the GeOₓ/Ge substrate using trimethylaluminum (TMA) and H₂O cycles because the ALD process provides a high uniformity and accurate thickness control layer by layer.¹⁹,⁹⁸-⁹⁹

However, the Al₂O₃ ALD process on GeOₓ/Ge surfaces has not been fully understood at the atomistic scale. In addition, effects of surface conditions (e.g., the bare, H-terminated, or oxidized Ge surfaces generally prepared in experimental conditions) on TMA/H₂O chemisorption have not yet been investigated. These factors can be attributed to the complex surface chemistry of Al₂O₃ ALD on Ge surfaces in nature. Thus, the present work aims to gain a fundamental understanding of growth kinetics of the Al₂O₃ ALD process on Ge surfaces using combined theoretical and experimental approaches. For the theoretical approach, a ReaxFF reactive force field for Ge/Al/C/H/O interactions was developed, and this potential was applied to investigating TMA and H₂O chemisorption on bare, H-terminated, and oxidized Ge surfaces. In addition, experimental work was carried out (from Dr. Engel-Herbert's research group in the Department of Materials Science at The Pennsylvania State University) using in situ spectroscopic ellipsometry (SE) analyses for real-time monitoring of Al₂O₃ ALD processes on the H-terminated and oxidized Ge surfaces. In this Chapter, a comprehensive study of the growth kinetics of Al₂O₃ ALD on Ge surfaces by experimental and theoretical methods is discussed.
5.2 Computational details

5.2.1 QM methods

As introduced, ReaxFF has been applied to study reactive events playing a critical role in the ALD process, which is central to microchip manufacturing. In order to develop a ReaxFF reactive force field to Ge/Al/C/H/O interactions, QM calculations were carried out for both periodic and non-periodic systems, and ReaxFF reactive force field parameters were optimized against the QM calculations. The QM calculations for the periodic systems in this work were carried out by Dr. George Psologiannakis, a former postdoctoral scholar of Dr. van Duin's group at The Pennsylvania State University. For the periodic systems, DFT calculations for 8 atoms of GeO and 9 atoms of GeO$_2$ unit cells were performed with the Vienna ab initio simulation package (VASP), using the GGA-PBE functional in the projector augmented-wave (PAW) method, a 500 eV energy cutoff, Gaussian smearing ($\sigma = 0.05$), and a $6 \times 6 \times 6$ Gamma-centered k-point grid. EOS were calculated by varying lattice parameters of the fully-optimized unit cell and performing ionic optimizations using the conjugate-gradient algorithm. Formation energies for two structures, GeO, and GeO$_2$, were evaluated with respect to the respective Ge diamond phases and the O$_2$ gas-phase based on the VASP optimizations of Ge and O$_2$ using the same computational choices. For the non-periodic systems containing Ge/Al/C/O/H interactions, the rapid ab initio electronic structure package of Jaguar (Version 8.3) with the B3LYP functional and LACV3P basis set was used to calculate bond dissociation and angle distortion energies for Ge/Al/C/H/O interactions, potentially allowing for chemical reactions between TMA/H$_2$O precursors and GeO$_x$/Ge surfaces.
5.2.2. Simulation setup

After developing the ReaxFF reactive force field for Ge/Al/C/H/O interactions, the ReaxFF potential was applied to simulate TMA and H$_2$O chemisorption on a variety of Ge surfaces. The surface models used for the ReaxFF calculations were as follows: (a) 60 Å × 60 Å × 10 Å of a bare Ge(100) surface, (b) 40 Å × 40 Å × 11 Å of a H-terminated Ge(100) surface, and (c) 40 Å × 40 Å × 20 Å of a GeO$_x$/Ge(100) surface. To evaluate reaction profiles for TMA/H$_2$O adsorption on the H-terminated Ge(100) and the GeO$_x$/Ge(100) surfaces, nudged elastic band (NEB)\textsuperscript{78} calculations were carried out by using the standalone ReaxFF code. Initial and final structures for all of the ReaxFF-NEB calculations were fully relaxed, and then four to six intermediate structures were generated for each ReaxFF-NEB calculation. Also, molecular dynamics (MD) simulations were carried out to assess reaction kinetics of the ALD process on the H-terminated Ge(100) and the GeO$_x$/Ge(100) surfaces using TMA/H$_2$O cycles. The H-terminated Ge(100) and the GeO$_x$/Ge(100) surfaces were placed in the orthogonal simulation boxes of size 40 Å × 40 Å × 50 Å, and 40 Å × 40 Å × 80 Å, respectively. Eighty-TMA or H$_2$O molecules were randomly distributed for each cycle (i.e., TMA/H$_2$O dose), and all of the gas phase molecules were removed for the next cycle. The sequence of the Al$_2$O$_3$ ALD on the GeO$_x$/Ge(100) surface for ReaxFF-MD simulations was as follows: the first TMA dose, second TMA dose, and first H$_2$O dose (up to 500 ps for each dose). The main reason for employing the second TMA dose prior to first H$_2$O dose was that there were a limited number of TMA precursors (80) during the first TMA dose, which was found to be insufficient to cover the single layer on the GeO$_x$/Ge(100) surface. Also, at the later stage of MD simulations, intact TMA molecules during the first TMA dose were not able to interact with the GeO$_x$ surface due to the formation of byproducts (C$_x$H$_y$ and CH$_4$) with a limited simulation box. Thus, all gas phase molecules were chosen to remove at the end of the first TMA dose, and then the second TMA
dose was performed to observe further TMA adsorption on the GeOₓ/Ge surface. For ReaxFF-MD simulations, the 28 June 2014 version of the LAMMPS code was used (http://lammps.sandia.gov), and the NVT ensemble using the Nose-Hoover thermostat with a damping constant of 25 fs was chosen to control system temperatures. It should be noted that the system temperatures used for the ReaxFF-MD simulations were relatively elevated (500 K for H-terminated Ge(100), and 1000 K for the GeOₓ/Ge(100) surfaces) as compared to experimental conditions (~543 K). This is because MD simulations can typically be performed with a limited time scale (~ ns) due to computational costs, and the time scale of the MD simulations was obviously much shorter than that of the experimental condition. As such, the present work performed ReaxFF-MD simulations with somewhat elevated temperatures to accelerate certain reactions and then to observe the complex surface chemistry.

Additionally, ReaxFF-MD simulations of O-diffusion from GeOₓ/Ge(100) and [Al₂O₃/GeOₓ]/Ge(100) interfaces were performed. Both interfaces were placed in the orthogonal simulation box (20 Å × 20 Å × 60 Å). For this analysis, the system temperature was kept at 300 K, while a relatively high temperature (800 K) was assigned to oxygen atoms to describe oxygen diffusion with a limited time frame (2.0 ns). All ReaxFF-MD simulations were performed with a time step of 0.25 fs to ensure the chemical reactions at given temperatures used in this study (300-1000 K). All of system configurations in this study were displayed using Molden 5.0 and VMD 1.9.2 software.
5.3 Results and discussion

5.3.1 Force field development and validation

ReaxFF reactive force field development

To correctly describe bulk characteristics of GeO$_x$ systems using the ReaxFF description, ReaxFF reactive force field parameters were trained against the formation energies and EOS for GeO and GeO$_2$ crystal structures. Figure 5-1 shows that ReaxFF fit to compression and expansion energies for the GeO and GeO$_2$ structures. The results indicate that the ReaxFF qualitatively reproduces the bulk characteristics of both GeO and GeO$_2$ structures. The ReaxFF reactive force field parameters were also trained against QM calculations of non-periodic clusters' interactions, including Al-C, Al-Ge, Ge-C, Ge-H, single Ge-O, and double Ge-O bond dissociation energies, and C-Ge-O, H-Ge-O, O-Ge-O, and Al-O-Ge angle distortion energies. (Figure 5-2 and Figure 5-3).

Figure 5-1. EOS for GeO and GeO$_2$ crystal structures obtained by ReaxFF and DFT calculations. Note that formation energies were calculated with respect to Ge-diamond and O$_2$-gas phases (Green colors represent Ge atoms and red colors represent O atoms).
Figure 5-2. ReaxFF fits to DFT calculations of Al-C and Al-Ge full bond dissociation curves. The Ge atoms are displayed in green, C in brown, H in white, and Al in sky blue.

The results showed that the ReaxFF description qualitatively agreed with the bond dissociation and angle distortion energies derived by the QM calculations. Furthermore, to give the ReaxFF description the ability to correctly mimic directions of reactions (i.e., endothermic or exothermic reactions) for TMA/Ge-related interactions, the ReaxFF reactive force field parameters were fit to QM calculations for the reaction energies being examined, as summarized in Table 5-1. It should be noted that as shown in Figure 5-2a, the Al-C bond strength of the ReaxFF value (~ 45 kcal/mol) underestimated that of the DFT value (~ 78 kcal/mol). This is because, the Al-O bond strength of the ReaxFF value (68 kcal/mol), based on the most recent Al/O description, was found to be weaker than that of the DFT value (~ 100 kcal/mol). Subsequently, the ReaxFF description was not able to correctly reproduce an exothermicity of "Ge(OH)$_4$ + Al(CH$_3$)$_3$ → Ge(OH)(CH$_3$)$_3$ +Al(OH)$_3$" in Table 5-1. However, it was impractical to retrain Al/O-related ReaxFF parameters at this stage, and thus, the Al-C bond strength was decided to be reduced when compared to the DFT value. As a result, the ReaxFF description for the above reaction quantitatively agrees with the DFT result (ReaxFF: -55.61 kcal/mol; DFT: -60.57). In the future, the ReaxFF potential can be refined by incorporating comprehensive training sets, including not only Al-O systems, but
also Ge/Al/C/H/O systems, thus improving the level of agreements between the ReaxFF and DFT values for both the Al-C and Al-O bond strengths.

Figure 5-3. ReaxFF fits to DFT calculations of bond dissociation and angle distortion energies for non-periodic clusters containing Ge/Al/C/H/O interactions: (a) Ge-C bond, (b) Ge-H bond, (c) single Ge-O bond, (d) double Ge-O bond, (e) C-Ge-O angle, (f) H-Ge-O angle, (g) O-Ge-O angle, and (h) Al-O-Ge angle. The Ge atoms are displayed in green, C in brown, O in red, H in white, and Al in sky blue.
In summary, the ReaxFF description developed in this work enables us not only to model GeO and GeO$_2$ crystal structures, but also to simulate the complex surface chemistry of TMA and H$_2$O chemisorption on Ge and GeO$_2$/Ge surfaces.

**Table 5-1 Reaction energies for TMA/Ge clusters' interactions, derived by DFT and ReaxFF calculations**

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Reaction Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ReaxFF (kcal/mol)</td>
</tr>
<tr>
<td>Ge(OH)$_4$ + C$_2$H$_6$ → Ge(OH)$_2$(CH$_3$)$_2$ + H$_2$O</td>
<td>59.04</td>
</tr>
<tr>
<td>Ge(OH)$_4$ + H$_2$ → Ge(OH)$_2$H$_2$ + H$_2$O$_2$</td>
<td>93.47</td>
</tr>
<tr>
<td>Ge(OH)$_4$ + Al(CH$_3$)$_3$ → Ge(OH)(CH$_3$)$_3$ +Al(OH)$_3$</td>
<td>-60.57</td>
</tr>
<tr>
<td>Ge(OH)$_2$O + H$_2$O → Ge(OH)$_4$</td>
<td>-74.01</td>
</tr>
<tr>
<td>AlGeH$_5$O$_6$ + H$_2$O → Ge(OH)$_4$ + Al(OH)$_3$</td>
<td>14.70</td>
</tr>
</tbody>
</table>

**ReaxFF reactive force field validation**

Essentially, the ReaxFF description for Ge/Al/C/H/O interactions was developed to model and simulate Al$_2$O$_3$ ALD on Ge surfaces using TMA and H$_2$O cycles. Thus, the ReaxFF should correctly describe kinetics associated with TMA/H$_2$O/Ge-related systems. For this reason, reaction paths for TMA and H$_2$O half reactions on H-terminated Ge clusters were calculated using the ReaxFF potential that had previously been conducted in DFT literature. As shown in Figure 5-4a-b, the results confirmed that ReaxFF had the ability to describe reaction paths for TMA and H$_2$O half reactions, which was qualitatively consistent with the DFT calculations.

In addition, to check if the developed ReaxFF description is capable of describing H migration along Ge bulk systems, we calculated H diffusion between two tetrahedral interstitial sites of a Ge crystal structure, as had been reported in DFT literature.
Figure 5-4. Comparison of TMA and H₂O half-reaction pathways on H-terminated Ge clusters between DFT and ReaxFF calculations (Ge: orange, Al: blue, C: green, H: white, and O: red).

The DFT study indicated that a reaction barrier along this path was about 0.3 eV, while ReaxFF-nudged elastic band (ReaxFF-NEB) calculations with three intermediate images yielded the reaction barrier of 0.45 eV (initial and final positions of H atom for this analysis are shown in Figure 5-5). These results indicated that the ReaxFF reactive force field developed in this study could be applied to capture the reaction path for H diffusion along Ge bulk systems with the reaction barrier, which was a qualitative agreement with the DFT value.
5.3.2 Analyses of Al₂O₃ ALD on Ge surfaces using TMA and H₂O cycles

As indicated in Section 5.1, the present work primarily focused on an atomistic-scale understanding of Al₂O₃ ALD on Ge surfaces, ultimately allowing for identifying optimal processing conditions to form a high quality of high-κ dielectrics/Ge-based semiconductors. For this purpose, ReaxFF studies of TMA and H₂O chemisorption on bare, H-terminated, and oxidized Ge surfaces are presented in this section.

TMA chemisorption on a bare Ge(100) surface

Figure 5-6a shows an initial configuration of the TMA chemisorption on a bare Ge(100) surface for the ReaxFF-MD simulations. To demonstrate the temperature dependence of TMA nucleation on a bare Ge(100) surface (60 Å × 60 Å × 10 Å), as previously conducted in open literature,¹⁰² ReaxFF-MD simulations were performed at 23, 227, and 427 °C. The analysis of simulation trajectories revealed that TMA molecules are non-dissociatively chemisorbed on Ge dangling bonds at room temperature (RT), whereas at high temperature (427 °C), residual methyl groups on TMA molecules either recombined to form methane (and ethane) or bind to
neighboring Ge dangling bonds, resulting in Ge-Al-Ge connections on the Ge(100) surface. The results are qualitatively consistent with scanning tunneling microscopy (STM) images (see Figure 5-6b).

Figure 5-6. Application of MD simulations demonstrating TMA nucleation on a bare Ge(100) surface: (a) initial configuration of 200 TMA molecules on a bare Ge(100) surface, (b) comparison of TMA nucleation on a bare Ge(100) surface as modeled by ReaxFF-MD and observed by STM,\textsuperscript{102} (c) estimated coverage of TMA sites obtained by ReaxFF-MD simulations (left panel) and determined experimentally using XPS (right panel).\textsuperscript{102} (STM images adapted with permission from ref.\textsuperscript{102} Copyright 2011 AIP Publishing LLC).

Additionally, the coverage of TMA sites with respect to the number of Ge dangling bonds was evaluated as a function of temperature and compared with X-ray photoelectron spectroscopy (XPS), as shown in Figure 5-6c. In summary, both theoretical and experimental approaches confirm that carbon coverage decreases with elevated temperatures due to the
dissociation of methyl groups from TMA, while Al coverage remains nearly constant, indicating that TMA sites become saturated under operating conditions.

**$\textit{Al}_2\textit{O}_3\textit{ALD on H-terminated Ge}(100)\textit{ surface}$**

Figure 5-7. (a) *in situ* SE monitoring of the $\textit{Al}_2\textit{O}_3\textit{ ALD on the H-terminated Ge}(100)$ surface; (b) AFM images of the H-terminated Ge(100) surfaces before and after the ALD processes.

Figure 5-7a shows the *in situ* SE monitoring of TMA/H$_2$O cycles on H-terminated Ge surface conducted by Dr. Engel-Herbert’s research group. The experimental study observed that $\textit{Al}_2\textit{O}_3$ growth in the early cycles (red dot square in Figure 5-7a) was lower than in later cycles, indicating the TMA nucleation delay on H-terminated Ge surface. As a result, the surface roughness of the Ge surface significantly increased during the ALD process, as confirmed by atomic force microscopy (AFM) studies shown in Figure 5-7b. These results suggested that TMA nucleation is delayed in the initial ALD cycles, and $\textit{Al}_2\textit{O}_3\textit{ ALD on H-terminated Ge surface}$ is non-conformal (*i.e.*, an island growth).
The TMA nucleation delay on a H-terminated Ge surface can be supported by our ReaxFF-NEB calculations. Figure 5-8a-b show reaction profiles for TMA/H$_2$O adsorption on H-terminated Ge surfaces and Ge dangling bonds derived using the ReaxFF-NEB scheme.

Figure 5-8. Reaction profiles obtained by the ReaxFF-NEB scheme for: (a) TMA adsorption (left) and H$_2$O adsorption (right) on the H-terminated Ge(100) and (b) the sequence of the TMA island growth on Ge dangling bond: TMA adsorption on a Ge dangling bond, H$_2$O adsorption on the Al(CH$_3$)$_2$ site, H$_2$O adsorption on the Al(CH$_3$)(OH) site, and TMA adsorption on Al(OH)$_2$ site. Note that the Ge dangling bond can essentially serve as a local center for the TMA island growth.
As shown in Figure 5-8a, reaction barriers of TMA (left panel) and H₂O (right panel) adsorption on H-terminated Ge(100) were found to be 1.41 eV and 2.89 eV, respectively, and overall reactions of the TMA and H₂O adsorption were exothermic by -1.09 eV and endothermic by 1.04 eV, respectively. These two factors indicated that both TMA and H₂O adsorption on H-terminated Ge surfaces were energetically unfavorable, leading to the initial nucleation delay on H-terminated Ge surfaces. That is, H-terminated Ge surfaces were chemically inert for both TMA and H₂O molecules.

To elucidate the mechanism for initializing TMA adsorption on H-terminated Ge surfaces, additional ReaxFF-NEB calculations of a reaction path for H diffusion on H-terminated Ge surfaces were performed; it was found that the reaction barrier of H diffusion into Ge sublayers was 0.68 eV, absorbing 0.39 eV energy for the entire reaction, as shown in Figure 5-9.

![Figure 5-9. ReaxFF-NEB calculations of H diffusion into the Ge sublayer and H₂ desorption from 2Ge-H⁺ on the top surface. The green circles represent Ge dangling bonds, obtained by H diffusion or H₂ desorption (The asterisk represents a surface species).](image)

Because such a reaction had a relatively low reaction barrier when compared to H₂ desorption from H-terminated Ge surfaces, the H diffusion into the Ge sublayer can be feasible at somewhat elevated temperatures in experimental conditions (~543 K), resulting in the formation of Ge
dangling bonds at the top surface. Consequently, the Ge dangling bond was expected to provide a local center for the TMA island growth. To verify this, TMA/H\textsubscript{2}O adsorption on the Ge dangling bond was divided into four processes in sequence: TMA adsorption on the Ge dangling bond, H\textsubscript{2}O adsorption on the Al(CH\textsubscript{3})\textsubscript{2} site, H\textsubscript{2}O adsorption on the Al(CH\textsubscript{3})(OH) site, and TMA adsorption on Al(OH)\textsubscript{2} site. Figure 5-8b shows the results of ReaxFF-NEB calculations of reaction profiles of the four processes above, which accounted for effects of the Ge dangling bond on the TMA chemisorption. These results clearly supported the TMA island growth mode locally around the Ge dangling bond as follows:

(1) TMA preferably chemisorbs on the Ge dangling bond, leading to the surface species of Ge-Al(CH\textsubscript{3})\textsubscript{2} and single CH\textsubscript{4} gas (see the first stage in Figure 5-8b). In addition, this reaction provides an additional Ge dangling bond at the neighboring site.

(2) Subsequent H\textsubscript{2}O doses hydroxylate the Ge-Al(CH\textsubscript{3})\textsubscript{2} site (the adsorbed TMA site), resulting in the surface species of Ge-Al(OH)\textsubscript{2} and CH\textsubscript{4} gases (see the second and the third stages in Figure 5-8b).

(3) At this stage, there are two available sites where TMA precursors preferably chemisorb: the newly formed Ge dangling bond and the Ge-Al(OH)\textsubscript{2} site that originates from the initial Ge dangling bond (see the fourth stage in Figure 5-8b). Additionally, as shown in Figure 5-10, the results of ReaxFF-MD simulations confirm that TMA preferably adsorbed only on the Ge dangling bond at the given temperature (500 K), and also H\textsubscript{2}O molecules only chose to bind on the Ge-Al(CH\textsubscript{3})\textsubscript{2} site.

In summary, the TMA island growth that was observed in the experimental work can be explained by the ReaxFF-NEB calculations and MD simulations. That is, the formation of the Ge dangling bonds served as the local center for the TMA island growth; thus, the Al\textsubscript{2}O\textsubscript{2} layer can be locally grown around the initial Ge dangling bonds.
Figure 5-10. Results of MD simulations at 500 K for: (a) 80 TMA molecules on a H-terminated Ge(100) surface with a single Ge dangling bond and (b) 100 H$_2$O molecules on the H-terminated Ge(100) surface with a Ge-Al(CH$_3$)$_2$* site (The red arrows refer to the Ge dangling bond). ReaxFF-MD results confirm that TMA and H$_2$O molecules preferably adsorb on the Ge dangling and Ge-Al(CH$_3$)$_2$* sites, respectively, rather than on H-terminated Ge sites.
Figure 5-11. (a) in situ SE monitoring of the Al₂O₃ ALD on the GeOₓ/Ge(100) surface; (b) AFM images of the GeOₓ/Ge(100) surfaces before and after the ALD processes.

Figure 5-11a shows the in situ SE monitoring of the Al₂O₃ ALD on the GeOₓ/Ge(100) surface. In this experimental study, it was found that there was a sharp rise in the thickness of the Al₂O₃ layer at the very first cycle, indicating that the GeOₓ/Ge(100) surface was active for TMA precursors. In the following four cycles, however, the Al₂O₃ growth was much lower than in the first cycle (see blue dot box in Figure 5-11a). In addition, as shown in Figure 5-11b, AFM measurements indicated that no significant surface roughening was observed during the Al₂O₃ ALD on the GeOₓ/Ge(100) surface when compared to the case of the H-terminated Ge surface (see Figure 5-7b). Based on these experimental results, we expected that: (1) H₂O would not only be an oxidant in forming the Al₂O₃ layer, but oxygen atoms in the GeOₓ layer would serve as primary oxygen sources during the early ALD cycles (i.e., a self-cleaning effect), lowering the further growth of the Al₂O₃ layer in the following several cycles and (2) after the self-cleaning effect, the TMA precursor evenly would chemisorb on the GeOₓ layer and then take oxidants from H₂O vapor, resulting in a high uniformity of Al₂O₃ layer in the later ALD cycles.
Figure 5-12. Results of TMA/H$_2$O dose on the GeO$_x$/Ge(100) layer described by the ReaxFF-MD simulations at 1000 K: (a) snapshots of the TMA/H$_2$O dose with changes in Ge-coordination numbers in the GeO$_x$ layer (Note: the number of Ge coordination was evaluated by only counting the number of O-bonds), (b) reaction barrier for TMA adsorption on GeO$_x$ layer described by the ReaxFF-NEB, (c) origin of O-sources in AlO$_x$ layer after first H$_2$O dose.

In order to further investigate growth kinetics of Al$_2$O$_3$ ALD on GeOx/Ge surfaces, ReaxFF-MD simulations of Al$_2$O$_3$ ALD on GeO$_x$/Ge(100) surfaces using TMA/water cycles were performed. The ReaxFF-MD simulation steps for TMA/H$_2$O cycles were as follows: the first
TMA dose, gas phase removal, the second TMA dose, gas phase removal, the first H$_2$O dose, and gas phase removal. Each step for the TMA or H$_2$O dose was performed up to 500 ps. Figure 5-12a shows snapshots of the initial GeO$_x$/Ge(100) slab after the first TMA dose, after the second TMA, and after the first H$_2$O dose, and changes in Ge-coordination numbers (counted by only O-bonds to Ge atoms) for each step. It was found that after the first and second TMA dose, TMA chemisorption occurred within GeO$_x$ layers widely; thus, GeO$_x$ layers turned into an intermixed AlO$_x$/GeO$_x$ layer. As a result, higher Ge-coordination numbers (5 or 4) in the GeO$_x$ layers were reduced to lower Ge-coordination numbers (3 or 2). These results demonstrate that TMA precursors can preferably take oxygen from GeO$_x$ layers to form the AlO$_x$ layer, thus leading to a decrease in oxygen levels in the GeO$_x$ layer (i.e., the self-cleaning effect). This effect can also be supported by the fact that, as shown in Figure 5-12b, TMA adsorption on GeO$_x$ surfaces has no reaction barrier and is highly exothermic (-3.02 eV). Subsequently, after the first H$_2$O dose, Al atoms continued to diffuse into the GeO$_x$ layer and there was a minor change in the Ge-coordination numbers: the 3-coordination number slightly decreases whereas the 4-coordination number slightly increases, indicating that H$_2$O hydroxylates Ge dangling bonds and/or the adsorbed TMA sites. Finally, Figure 5-12c shows that oxygen sources in AlO$_x$ layers originated from 91.4% of the GeO$_x$ layer and 8.4% of H$_2$O, leading to the intermixed AlO$_x$/GeO$_x$ layer during the early ALD cycles. These facts explain well how the self-cleaning effect can be achieved during the early ALD cycles. Based on the results of ReaxFF-MD simulations, we confirmed that the GeO$_x$ surface was chemically active for TMA precursors, thus leading to the self-cleaning effect and the conformal ALD process.

Additionally, effects of the Al$_2$O$_3$ ALD on thermal stability of the GeO$_x$/Ge(100) layer were investigated. Figure 5-13 shows the results of ReaxFF-MD simulations for the comparison of thermal stability on GeO$_x$/Ge(100) and [Al$_2$O$_3$/GeO$_x$]/Ge(100) interfaces. In the case of the GeO$_x$/Ge(100) interface, a relatively large portion of oxygen atoms diffused from the GeO$_x$ layer
into the Ge subsurface. In contrast, oxygen diffusion into the Ge subsurface was suppressed by the existence of an Al$_2$O$_3$ layer on the GeO$_x$/Ge(100) interface. Thus, it can be suggested that the oxygen diffusion into Ge subsurface can be delayed by incorporating the Al$_2$O$_3$ layer on the GeO$_x$/Ge surface. Please note that in case of the GeO$_x$/Ge slab, no further oxygen diffusion into a deeper Ge-bulk phase was observed at given simulation conditions (a system size and a time scale). To further investigate the effect of the Al$_2$O$_3$ layer on the thermal instability of the GeO$_x$/Ge slab, a larger subsurface and a longer MD simulations should be carried out in the future.

Figure 5-13. The results of the ReaxFF-MD simulations of oxygen diffusion from GeO$_x$ into the underlying Ge subsurface for GeO$_x$/Ge(100) (red curve) and [Al$_2$O$_3$/GeO$_x$/Ge(100) (black curve) interfaces. The portion of oxygen diffusion was normalized by the total number of oxygen atoms in the GeO$_x$ layer.
5.4 Chapter Summary

In Chapter 5, comprehensive studies on TMA and H₂O adsorption on Ge surfaces were reported theoretically and experimentally in order to investigate the complex surface chemistry of the Al₂O₃ ALD process. The results can be summarized as follows:

- The ReaxFF potential for Ge/Al/C/H/O interactions developed in this work demonstrated the ability to correctly describe the TMA chemisorption on the Ge surface, which is qualitatively consistent with the experimental literature available.
- The combined ReaxFF and experimental studies revealed that the Al₂O₃ ALD on H-terminated was found to be non-conformal, thus resulting in defective dielectric/semiconductor interfaces, while the self-cleaning effect was found during the Al₂O₃ ALD on GeOx/Ge surfaces, thus leading to less defective dielectric/semiconductor interfaces with enhanced thermal stability.
- The present study’s findings suggest optimal conditions for manufacturing Ge-based CMOS devices: using the ReaxFF potential will allow us to assess the Al₂O₃ ALD process with different factors such as temperature, pressure, and system size.
Chapter 6

Conclusions

In order to gain atomistic-scale insights into growth kinetics of Al2O3 layers on bare and carbon-coated ANPs and Ge-based semiconductors, the ReaxFF reactive force field method was used in this work. Detailed strategies for the above-mentioned studies were: (a) ReaxFF-molecular dynamics (ReaxFF-MD) simulations of the oxidation of bare ANPs were performed using the ReaxFF potential for Al/O interactions; (b) a ReaxFF reactive force field for Al/C/H/O systems was developed by optimizing against quantum mechanics-based (QM-based) training sets, and the developed ReaxFF potential was applied to understanding reaction events between ANPs and hydrocarbon with oxygen environments; (c) the ReaxFF potential was further extended to Ge/Al/C/H/O systems using QM-based force field training, subsequently allowing for studying the surface chemistry of Al2O3 atomics layer deposition (ALD) processes on Ge surfaces. The conclusions drawn from the present work are in the following:

i. The ReaxFF potential for Al/O systems is capable of performing MD simulations of the oxidation of bare ANPs at elevated temperatures (~ 900 K), enabling an explanation of the mechanism of the oxidation process on ANPs from an atomic-scale viewpoint. That is, the void space, derived by a highly exothermic reaction, lowers the reaction barrier for oxygen diffusion between two Al-tetrahedral sites and thus, primarily accelerates the oxygen diffusion into the core of ANPs.

ii. The newly developed ReaxFF potential for Al/C/H/O systems has the ability to describe interaction between ANPs and hydrocarbon, as well as the oxidation of carbon-coated ANPs. The ReaxFF studies enabled assessment of the full dynamics of such reactions with
theoretical support (i.e., reaction barriers and energies), thus making it possible to understand the effects of carbon coating on the oxidation kinetics of the ANPs.

iii. The ReaxFF potential for Ge/Al/C/H/O systems developed in this work demonstrated the TMA island growth and the self-cleaning effect on H-terminated Ge surfaces and GeOx/Ge surfaces, respectively, as shown in comprehensive experimental work. Such a collaboration between experimental and theoretical approaches eventually allows us to manufacture less defective high-κ/non-Si semiconductor interfaces.

Furthermore, future work can be suggested to extend applications of the ReaxFF potential that has been developed in this study as follows:

i. Additional MD simulations of aggregation of bare and carbon-coated ANPs can be performed to elucidate the effect of carbon coating on aggregation kinetics of ANPs. This study will explain how the coating layers lower a surface cohesiveness of ANPs, and subsequently how much they prevent the degree of agglomerations during the combustion process.

ii. Effects of thickness of the carbon coating layer on the oxidation kinetics can be considered as an additional case study. Because this study demonstrates that the carbon coating effectively controlled the oxidation of ANPs as a function of temperature, it can be expected that the thickness of the carbon coating on the ANP surface will affect the level of the oxidation of ANPs at given temperatures. Thus, MD simulations of the oxidation of ANPs after different numbers of hydrocarbon coating processes would provide a better idea on reaction kinetics between the coating layer and oxygen molecules.

iii. According to experimental literature, hydrocarbon precursors can ultimately form graphitic layers on ANPs after laser-induced complex heating processes. As such, the ReaxFF potential can be extended to graphene/ANPs systems, making it possible to model single or multi graphitic-layered ANPs. This approach will present very interesting results
such as the oxidation kinetics of ANPs as a function of numbers of graphitic layers on the surface of ANPs. The ReaxFF potential for graphene/ANPs systems would also suggest new ideas on modeling combined carbon and ANPs composites such as ANPs-introduced graphite systems, which can be considered as "effective nano-scale energetic formulations" for the solid propellants.

iv. Large scale (massively parallel) and long-time scale MD simulations of $\text{Al}_2\text{O}_3$ ALD processes on the GeO$_x$/Ge surface can be suggested as follows: (1) TMA half cycles with different system temperature to understand the saturation level of TMA precursors and the removal of hydrocarbon species as a function of temperature; (2) TMA half cycles with different gas pressures to investigate the effect of the TMA gas pressure on the TMA nucleation; (3) TMA/H$_2$O cycles with different thicknesses of the GeO$_x$ layer to provide ideal surface conditions for manufacturing fine $\text{Al}_2\text{O}_3$ passivation layers.

v. Finally, the ReaxFF potential can be extended and developed for additional complex systems related to the ALD processes. In other words, it is feasible for the ReaxFF description to model multi-layer gate stacks, such as a HfO$_2$/Al$_2$O$_3$/GeO$_x$/Ge system, and simulate the ALD process using other possible precursors besides TMA molecules. These studies will enable us to perform full dynamics of multi-layer high $\kappa$/Ge gate stacks, and to suggest effective gas precursors for the ALD process.

Therefore, this dissertation provides a future guideline for further investigation of reaction kinetics and surface chemistry for a wide range of nano-scale systems. That is, by collaborating with experimentalists, the ReaxFF reactive force field method can identify promising candidates for surface passivation on not only metal nanoparticles but also other semiconductor interfaces. By doing so, high-performance solid propellants and high-quality high-$\kappa$/non-Si based semiconductors can be made possible and applied to next-generation technology.
To conclude, it is believed that the ReaxFF potential will provide a powerful and reliable computational tool for modeling complex nano-scale systems in the future.
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