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Ractive MD Simulation on the Formation of Amorphous Alumina Layer Using Atomic Layer Deposition (ALD)

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**REACTIVE MD SIMULATION ON THE FORMATION OF AMORPHOUS ALUMINA
LAYER USING ATOMIC LAYER DEPOSITION (ALD)**

A Master's Thesis

Presented to

The Graduate College of

Missouri State University

In Partial Fulfillment

Of the Requirements for the Degree

Master of Science, Materials Science

By

Yuxuan Lu

August 2020

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REACTIVE MD SIMULATION ON THE FORMATION OF AMORPHOUS ALUMINA LAYER USING ATOMIC LAYER DEPOSITION (ALD)

Physics, Astronomy and Materials Science

Missouri State University, August 2020

Master of Science

Yuxuan Lu

ABSTRACT

In this study, a systematic study has been performed by using the large-scale classical reactive molecular dynamics (MD) simulations to model the Atomic Layer Deposition (ALD) processes that generated an ultra-thin and sub-nano meter amorphous alumina. The ALD process employed both water pulse and (Trimethyl-Aluminum) TMA precursors deposited onto the surface of an aluminum wetting layer. The study varied the sizes of the substrate and the concentrations of water/hydroxide precursors with a range of operating temperature to design the most favorable configurations for the subsequent TMA precursors to add onto. The role of crystallographic orientation of the Al wetting layer was also investigated and compared. Advantages and limitations in using the reactive interatomic potentials of ReaxFF were identified and correlated with the observations obtained from the MD simulations.

KEYWORDS: Molecular Dynamics, Atomic Layer Deposition, ReaxFF Potentials, Alumina, TMA

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August 2020

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In the interest of academic freedom and the principle of free speech, approval of this thesis indicates the format is acceptable and meets the academic criteria for the discipline as determined by the faculty that constitute the thesis committee. The content and views expressed in this thesis are those of the student-scholar and are not endorsed by Missouri State University, its Graduate College, or its employees.

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I dedicate this thesis to Moling Yuan, Jing Lu, and Yunfei, Lu.

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INTRODUCTION

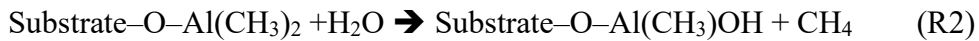
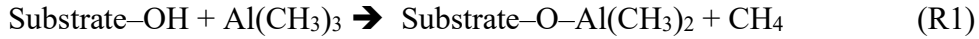
Atomic Layer Deposition (ALD)

Atomic layer deposition (ALD) is a coating technology which is universally used for the construction of highly uniform thin films. It has emerged as an important technique that materials can be plated on the surface of substrate one by one in the form of monatomic film ¹ for a variety of applications. However, in the process of atomic layer deposition, the chemical reaction of a new layer of atomic film is directly related to the previous layer. This way, only one layer of atoms is deposited in each reaction. Thin films are formed by alternately and repeatedly introducing gas precursor pulse into the reactor and chemically adsorbing and reacting on the deposition substrate. At present, when the drive reaches the surface of the substrate, they will chemically adsorb and react on the surface. It is necessary to clean the atomic layer deposition reactor with inert gas between the precursor pulses. The self-limiting growth mechanism enables a highly uniform and the thickness can be controlled accurately at the atomic level. ² The key to realize the atomic layer deposition is whether the precursor material can be chemically adsorbed on the surface of the deposited material, so it is very important to select the appropriate reaction precursor materials to achieve the atomic layer deposition.

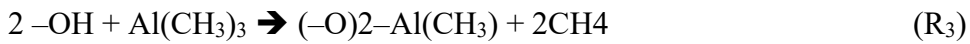
Among the most studied ALD-process, the repeated cycles of trimethylaluminium (TMA) + water process forming the alumina (Al_2O_3) is a popular ALD technique. Here, the process uses (1) TMA and (2) water as the two precursors for each ALD cycle. The main advantage in choosing these two precursors is because they ideally create self-terminating adsorption processes and the reaction by-product methane is inert in the reacting processes. The initial reactions in the process and reaction pathways has been studied by Weckman and

Laasonen ¹. In their study, band gap of the produced Al₂O₃ thin film is 9 eV which shows that the product is a dielectric material with a moderate permittivity.

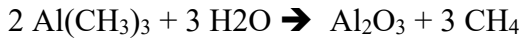
Since there are two precursors, TMA and water, the process can be presented with two “half-reaction”, one for the TMA-pulse toward the hydroxylated substrate (“Substrate-OH”) and another one for the water-pulse:



where (R1) is the reaction with only one hydroxide while the reaction can also be proposed with two hydroxide groups



The overall reaction of the process is



Weckman and Laasonen ¹ also show the surface process using density functional theory (DFT) with their detailed energetics of the hydroxideated surface during the TMA pulse with the use of dimethylaluminium (DMA) and monomethylaluminium (MMA) as the end-products of the TMA pulse. Despite the DFT work done already to model the key mechanisms of ALD processes based on the reaction sequences above, there is a very limited study that has been done to model the process at atomistic scale at operating temperatures (typically at room temperature to 200°C). The work by Weckman and Laasonen ¹ for example was conducted at the ground state (OK) and involved less than a hundred of atoms. This is because the DFT calculations are generally expensive. Thus, there is a need to extend these types of calculations beyond DFT simulations, for example, by using classical molecular dynamics (MD) simulations.

Amorphous Alumina

Amorphous alumina (a- Al_2O_3), a multifunctional material, has a promising prospect with its properties in electrical and catalytic as well as its oxidation and corrosion resistance.³ The a- Al_2O_3 films shows its advantage especially in microelectronic devices due to its low leakage current and high dielectric constant. Therefore, the research of the structure of a- Al_2O_3 thin films has been warmly welcomed in recent years since it can significantly influence the design of new materials and devices where this phase exists.

In general, the alumina has many technological applications and the production technique for each application can vary a lot. For example, the alumina can also be used as compact hard protective coatings and high specific surface area supports for catalysis produced by Pulsed laser deposition (PLD)^{4,5} under the varying oxygen pressure. The ALD process mentioned above is intended to generate an amorphous alumina layer that can be used as a tunnel barrier layer in a tunnel junction fabrication process. The ALD process, a form of chemical vapor deposition (CVD) in this case, with its self-limiting growth capability, is quite unique in that the layer thickness of the alumina can potentially be carefully controlled so that the tunnel barrier layer can also be well controlled.⁶

As a crystalline, the alumina oxide (Al_2O_3), is a dense material with a high hardness with a melting point is 2054 °C and boiling point is 2980 °C. The crystalline Al_2O_3 phase has more than 10 homomorphic and heterogeneous crystals, and the three main crystal types are α - Al_2O_3 , β - Al_2O_3 and γ - Al_2O_3 . Among them, the structure is different, and almost completely transformed into α - Al_2O_3 at high temperature above 1300 °C as the most stable phase. The main product obtained by the ALD process however is not crystalline, but an amorphous phase which is generally less dense/more porous and often with many types of defects. Even though the

ALD deposition process creates self-terminating layer depositions, it does not mean that the layer will be dense and packed especially at the initial stage of the ALD process. The quality of the amorphous alumina layers during the first ALD cycle will depend very much on the adsorption mechanism of the precursors to the substrate. Thus, there are recent works done to improve the quality of the alumina layer by adding a close packed metallic layer like aluminum (the “wetting layer”) before the ALD process so that the first layer of water or OH can be made highly dense.

Aluminum as a Wetting Layer

Aluminium is of significant technological importance in some scientific areas, with its unique ability to form compounds with different elements, and the special structure of the compounds. An aluminium atom has 13 electrons, which arranges like the configuration of $[\text{Ne}]3s^2 3p, ^7$ with 3 electrons are left outside that can be easily surrender in oxidation. Aluminium atoms connect to each other by metallic bonding forms by the conduction electrons and form a close packed structure: face-centered cubic. Since few electrons are available for metallic bonding, aluminium metal is soft with a low melting point and low electrical resistivity. The melting point (933.473 K, 660.323 °C) ⁷ of aluminium is low because there are few electrons that can be used for metallic bonding, which lead to the softness of aluminium metal. This property also helps aluminum to be easily used as a metallic coating. The density of aluminium is 2.70 g/cm³ and its crystal structure is a close-packed face-centered cubic (fcc) crystal structure and its lattice parameter of ~0.405 nm. Like other FCC metals, a crystalline Al layer will deposit with a preferred orientation of (111) plane as the most packed atomic plane within the crystal structure.

Classical MD Simulation

Molecular Dynamics (MD) is a comprehensive technology combining physics, mathematics and chemistry. It is a set of molecular simulation methods, which mainly relies on Newton's equation of motion to simulate the movement of molecular system. It is used to simulate interactions between atoms in real life using computer modeling: taking samples from the system composed of different states of the molecular system to calculate the configuration integral of the system, and further calculate the thermodynamic quantity and other macro properties of the system based on the results of the configuration integral.

In a classical MD model, atoms are confined in a simulation with a certain region and a predetermined period of time, so the interaction between atoms can only be shown in the defined space and time period. The initial position of atoms, velocity, force and other basic information are needed as the input in Classical MD simulation so as to obtain the trajectory of the system by solving Newton's equation of motion.

$$m_i \frac{\delta^2 r_i}{\delta t^2} = F_i$$
$$F_i = - \frac{\delta U(r_1, \dots, r_n)}{\delta r_i}$$

where U is the potential of the system in a given configuration, m_i is the mass, F_i the force and r_i is the position of i -th object of a system with n object in total. The choice of action potential is closely related to the calculation of dynamics. With different action potential, the potential energy surface of the system will have different shapes which leads to different molecular motion and the trajectories of the internal movement of molecules and will further affect the results of sampling and its potential energy. For example, when calculating the relationship between the macro volume and the micro components, the two-body potential of the rigid sphere model is mainly used, and Lennard-Jones potential and Morse potential are mostly used when

calculating the relationship between the system energy and entropy. When calculating the three-body force, Tersoff and Stillinger-Weber potential are used. Apart from these, EAM potential is universally used in many-body force and spring potential used in calculating molecular force. After the suitable potential U is decided, the trajectory of a system can be calculated by the equations. In practice, the equation sets are replaced by the integration to save time in computational calculation.⁸

$$-m_i \frac{dv_i}{dt} = \sum_j F_2(r_i, r_j) + \sum_{j, k} F_3(r_i, r_j, r_k) + \dots \dots \dots$$

$$\frac{dr_i}{dt} = v_i$$

Here, F_n is the force between n atoms. The position and the force information of the atoms are adjusted after each iteration and the calculation repeats afterwards. The approximations are a little bit more accurate since the time–evolution of the system has been fully described in these equations, in other words, the dynamic behavior of the atomic system is described empirically without having to solve Schrodinger’s equation at each timestep, which leads to a great computational advantage compared to ab-initio calculations.

MD simulation can be used in the calculation of NPT, NVE, NVT and other systems. It is a thermodynamic calculation method based on the determinism of Newton’s equation. Compared with Monte Carlo method, it has higher accuracy and effectiveness in the calculation of macro properties and can be widely used in physics, chemistry, biology, materials, medical and other fields.

Reactive Interatomic Potential of ReaxFF

The reactive force-field (ReaxFF) is a bond order-based force field for the simulation of chemical reactions with atomic potentials developed by Adri van Duin and coworkers at the California Institute of Technology.⁹ The ReaxFF method was developed to help bridge the gap between the quantum mechanics (QM) and empirical interatomic potentials.

Methods based on the principles of QM, while applicable to most of chemical systems, are generally of too computational expense and too time-consuming for simulations that makes them inapplicable for large systems and high-temperature MD simulations. Empirical interatomic potentials, basing on classical principles, can describe interactions with a set of relatively simple potential functions so significantly fewer computational resources are required in the simulation.¹⁰ Therefore, these methods can better describe the dynamic processes with longer timeframes and larger modeling scales than QM systems (thousands of atoms on single processors; millions of atoms on multiprocessors).

In order to be able to handle bond breaking and formation in the case when each element has only one single atom type, ReaxFF has many parameters including potentials such as Coulomb and Morse (van der Waals) potentials that are used for describing nonbond interactions between all atoms, bond and angle stretches, valency angle, activation and reaction energies, electronic structure, surface energies, and so on. With the calculation of the general relationship between bond distance (interatomic distances) and bond order used by ReaxFF force field, we can derive a proper dissociation of bonds to separated atoms as well as their interatomic potential.¹¹

ReaxFF has many applications as shown in figure 1. One of the most important applications of ReaxFF is MD simulations. ReaxFF makes it possible for the description of each element transformable across phase so that it is able to describe and simulate the reactions at the

interface between solid, liquid, and gas phases, both for the same or different elements. This allows ReaxFF to consider the phenomena such as diffusivity and solubility which dependent

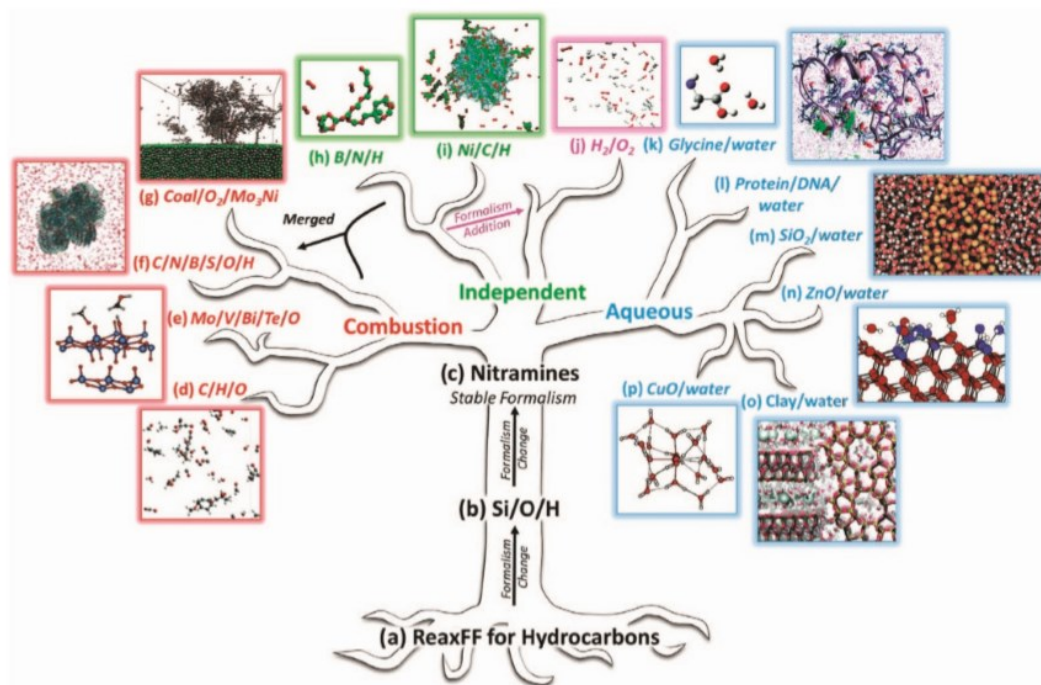


Figure 1. A wide range of applications of ReaxFF.¹⁰

on dynamic factors affecting the migration of each species in the system. These advantages above, lower computational expense, longer simulation timescales and the phase transferability, make the ReaxFF a good choice for simulating large model with complex processes and longer timescale involving multiple phases.

As mentioned previously, ReaxFF uses the bond-order formalism as well as polarizable charge descriptions to describe how the atoms within the system will interact with each other both reactively. The system energy can be described by the energy contributions of these partial energy and the expression is shown below.

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{tors}} + E_{\text{coa}} + E_{\text{conj}} + E_{\text{vdWaals}} + E_{\text{Coulomb}} \quad 12$$

These partial contributions are due to the bond order and bond energy, atom under-/over coordination stability, valence angle and torsion, nonbonded van der Waals interactions and coulomb interactions.

Calculating Bond Order. The first step after recording the initial positions of each atom in the system is to determine the bond order between each atom pair which can be performed empirically direct from interatomic separation. The potential should be considered including both bond order dependent and independent components. The bond order interaction can be calculated by this given equation:

$$BO_{ij} = BO_{ij}^{\sigma} + BO_{ij}^{\pi} + BO_{ij}^{\pi\pi}$$

$$or, BO_{ij} = \exp \left[p_{bo1} \left(\frac{r_{ij}}{r_o^{\sigma}} \right)^{p_{bo2}} \right] + \exp \left[p_{bo3} \left(\frac{r_{ij}}{r_o^{\pi}} \right)^{p_{bo4}} \right] + \exp \left[p_{bo5} \left(\frac{r_{ij}}{r_o^{\pi\pi}} \right)^{p_{bo6}} \right]$$

where the first exponential terms determine the single bond order contributions, the second, and the third, exponential terms determine the double (pi bond), and triple (double pi bond) bond order contributions, respectively.

The result of the calculation should be adjusted and corrected because due to long range interactions, the attraction/bond order with its second nearest neighbor is weak and will lead to unrealistic behavior. This equation shows the bond energies from the corrected bond order BO_{ij} .

$$E_{bond} = -D_e \cdot BO_{ij} \cdot \exp \left[p_{bo1} \left(1 - BO_{ij}^{p_{be,1}} \right) \right]$$

Atom Under-/Overcoordination. An overcoordination penalty term has been added to the force field to correct the overcoordination that may remain in the molecule.

$$E_{over} = -p_{over} \cdot \Delta_i \cdot \left(\frac{1}{1 + \exp (\lambda_6 \cdot \Delta_i)} \right)$$

$$E_{under} = -p_{under} \cdot \frac{1 - \exp (\lambda_7 \cdot \Delta_i)}{1 + \exp (-\lambda_8 \cdot \Delta_i)} \cdot f_6(BO_{ij,\pi}, \Delta_j)$$

Apart from these terms, the Valence Angle Terms including angle energy and three-body conjugation term, the four body conjunction term and hydrogen bond interactions are also very important and should be taken into consideration in the calculation of the system energy.

PACKMOL

The first step of the MD simulation is to create the particles and put them in the suitable place to make sure they would have a proper interaction. PACKMOL code is usually used in randomly creating atoms or molecules in a definite size of space in the simulation cell before MD simulation.¹³ It mainly creates gaseous mixture or amorphous structures.

Adequate initial configurations is of great importance for MD simulations since there are repulsive interactions by large van der Waals force, the atoms from different molecules must keep safe distances and do not crash each other. After the right geometrical constraints of each type of molecule are provided and the region of the molecules is given, PACKMOL can randomly arrange the molecules in the region which may be intersections of spheres, ellipses, cylinders, planes, or boxes, and show the coordinates in the three-dimensional space.

Molecular Dynamics Code of LAMMPS

Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS), distributed by Sandia National Laboratories, a US department of energy laboratory, is a classical molecular dynamics code which focus on materials modeling for classical MD system on different scales. LAMMPS has potentials in modeling many kinds of materials including not only solid materials such as metals and semiconductors, but also liquid or gaseous phase and even the combinations of these phases.

LAMMPS can model a variety of materials with a large range of scale from a few particles to millions or billions in a 2-dimensional or 3-dimensional system as long as given suitable inputs and enough time. It has a large potential in application because it can not only be applied in many kinds of materials including soft matter (biomolecules, polymers) and coarse-grained or mesoscopic systems, but also applied in the simulation of atomic, microscopic, mesoscopic, or continuous scale. A variety of interatomic potentials (force fields) and boundary conditions can be used in modeling for different systems such as atomic, polymeric, biological, solid-state (metals, ceramics, oxides), granular, coarse-grained, or macroscopic systems.

LAMMPS can be run on any parallel machine supporting the Message Passing Interface (MPI) library including a laptop or desktop but it will take a long time if the scale of the module is large or the input simulation time step is large. In LAMMPS model, a particle which can be an atom, electron, molecule, cluster of atoms or clump of material, is simulated with the use of Newton's equations of motion to derive the interacting behaviors and the interaction models are either short-range models as mostly found in nature, or some long-range models.

In this work, the models are of different size and scale, from hundred atoms to billions of atoms, and the particles are in different phase, solid, liquid and gas. In this case, LAMMPS is a good choice for the MD simulation.

Simulation Suite of ADF

The computational chemistry program Amsterdam Density Functional (ADF), which was first developed by the group of E. J. Baerends from the Vrije Universiteit in Amsterdam and the group of T. Ziegler from the University of Calgary, is a powerful program using molecular density functional theory (DFT) for the calculations of for first-principles electronic structure

that helps understanding chemistry reactions. In the nineties, the development and distribution of ADF has been coordinated by the Software for Chemistry & Materials (SCM) company.

Together with the increasing use of DFT in the calculation of computational chemistry, ADF has become more and more popular. ADF excels in understanding and predicting structure, reactivity, and spectra of molecules with the help of DFT calculation, particularly in studying transition metal complexes and heavy elements problems and all elements in the periodic table can be modeled accurately and efficiently. SCM also provide a ReaxFF Manual and a set of GUI tutorials helping users making the models and doing the simulations.

The program can not only used for ADF and DFT, but also for BAND (a periodic structure counterpart of ADF), DFTB (a density-functional based tight binding), ReaxFF, Mopac, Quantum ESPRESSO, COSMO-RS more.

ADF is a graphical interface consists of several modules with parallel binaries and integrated GUI, which helps to predict molecular properties of nanoparticles and organic electronics materials. In these models, ADFinput is to set up calculations and ADFview to visualize orbitals. With these modules work together, DFT calculations are easily prepared and analyzed.

In this work, we use NVT dynamics and ReaxFF for the MD-simulation systems. The temperature can be controlled using the tregime.in file in which we can increase or decrease the system temperature within a certain timescale and the system can be divided to different parts for the application of different temperature regimes during an MD-simulation.

COMPUTATIONAL DETAILS

In this study, we focus on large-scale classical reactive molecular dynamics (MD) simulations of ALD processes to model the formation of amorphous Al_2O_3 using TMA and H_2O cycles as a route for developing Al-based metal oxide devices. We are trying to demonstrate the temperature dependence of the deposition. We varied the sizes of the substrate and the concentrations of water/hydroxide precursors with a range of temperature to design the most favorable configurations for the subsequent TMA precursors to add onto.

Both LAMMPS and ADF are used for simulating this ALD process and in both cases, we change the size of the model, orientation of the aluminum substrate and the simulation temperature.

LAMMPS Simulation

Building the module is very important which has an influence in all procedures that follow. In the LAMMPS simulation, all the input atom position must be prepared separately and all the input information such as atom position, input file, input control file and the ReaxFF force field files should be put in the same directory before the simulation. The reactive forcefield we chose the ReaxFF of Al/C/H/O made in 2011 by Aidan Thompson according to the MD simulations of hydrocarbon oxidation research by Chenoweth, van Duin and Goddard in 2008.¹⁴ And the code is shown in Appendix A.

Before all the simulation, we did the minimization to the molecules with the LAMMPS code:

```
minimize 0.0 1.0e-8 1000 100000
```

We relax systems to minimize the interaction between atoms by iteratively adjusting atom coordinates, the code is shown in Appendix B. This means the coordinates of atoms changes and the energy between the atoms calculated till reach the minimum value. Then the configuration should be expected to approximate a critical point which the local potential energy is minimum. Because of the large energies and forces exist between the atoms when they are too close to each other, the movement of the atoms are limited by the minimizer and when there are highly overlapped atoms, they will be pushed from each other.

Figure 2 shows the visualize of each type of atoms and molecules that will be added to our system, where the pink one is aluminum, the blue one is oxygen, the yellow one is hydrogen and the green one is carbon.

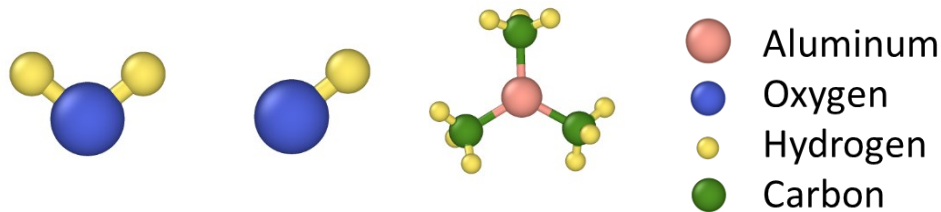


Figure 2. Precursors and the atom type: H_2O , OH and TMA.

The first step to build a module in our simulation is to build the substrate. We can use ovito and other computational materials such as USPEX to make the substrate with a suitable scale. In this work, we mainly focus on the Al substrate with two orientations, Al(100) and Al(111), and there are 1296 Al atoms in both modules separately. Figure 3 and 4 shows the structure of the two substrates.

In these figures, it is obvious that the configuration of the surface of Al is different in different configuration so for different structure. The plane density of Al(111) is larger than that of Al(100), and there are 11 nearest neighbors left for the surface atoms in Al(111) while there

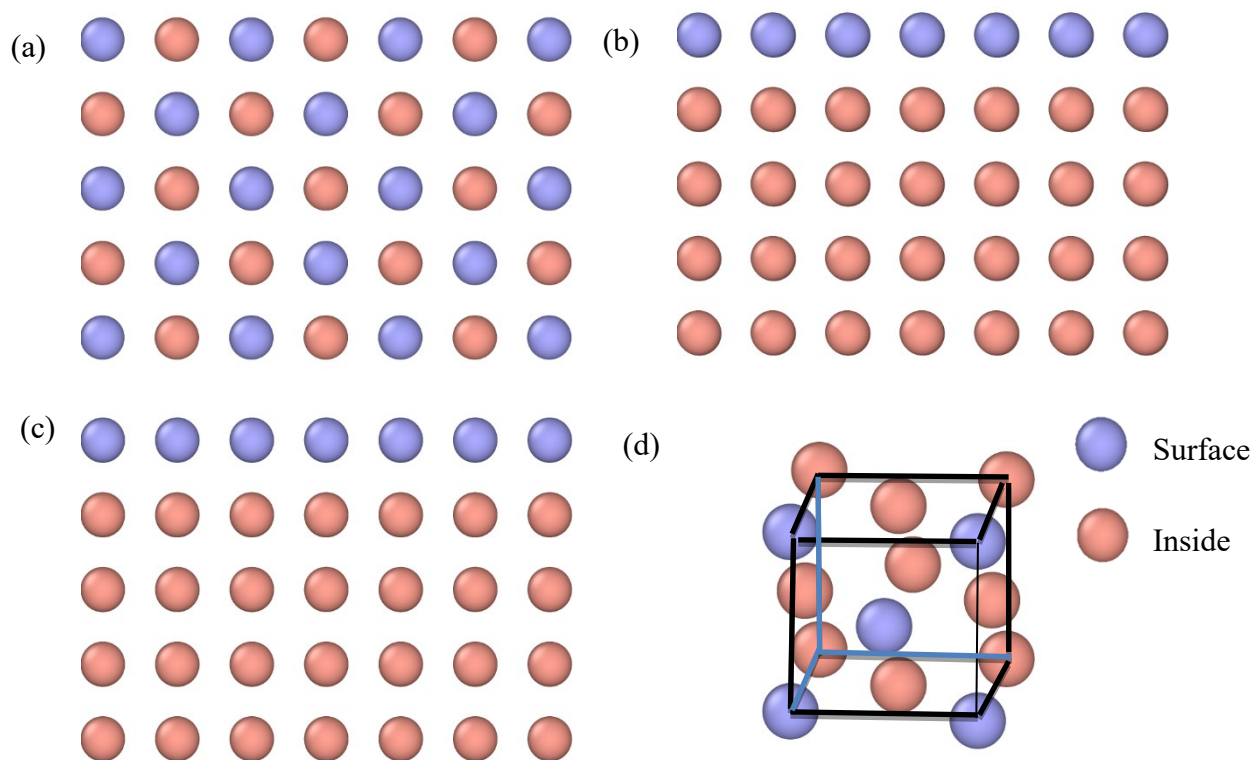


Figure 3. Structure of Al(100) seen from (a) z-direction, (b) y-direction and (c) x-direction and (d) as a unit cell.

are only 8 nearest neighbors left for the surface atoms in Al(100). The surface energy which effects the adsorption of the water and hydroxide precursors may be also different. It may lead to different ability of adsorption of molecules on the surface and different stability of the substrate. After building the substrate, we need to put the precursor randomly above the surface of the substrate inside the simulation cell with a minimum distance 2 angstroms between molecules. PACKMOL code is used in this step since it can randomly put the molecules as well as avoid the

overlapping of atoms. Above both Al(100) and Al(111) substrates, 18 H₂O molecules or 18 OH molecules are put as the precursor separately to compare the ability of adsorption at 300K. We then increase the temperature of the module with Al(111) substrate and OH precursor which shows the best adsorption while maintaining the stability.

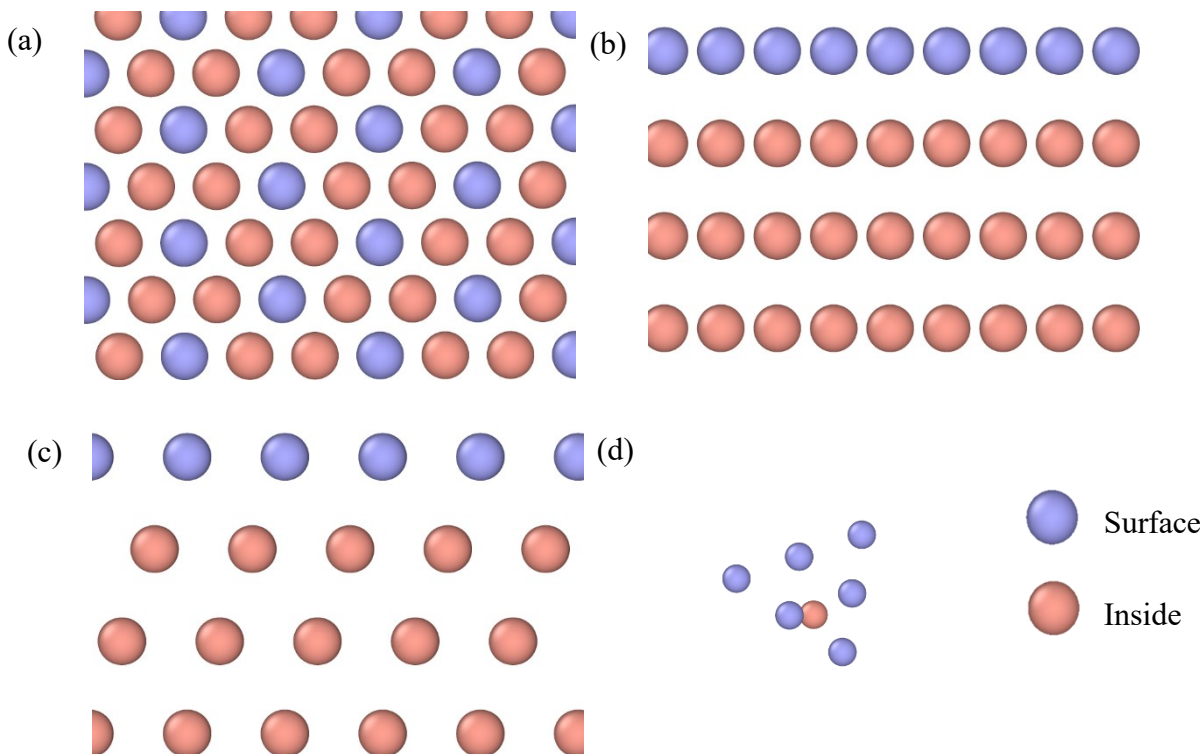


Figure 4. Structure of Al(111) seen from (a) z-direction, (b) y-direction and (c) x-direction and (d) as part of a unit cell.

The next is to put the second precursor, TMA, on the top of the module which performs best with PACKMOL code. The temperature is also increased to observe the temperature independence behavior of the system. It is expected to see that with the temperature increases, the reaction between the OH and TMA would accelerate. However, it is possible that the substrate would melt, or the molecules decompose when the temperature goes too high.

To avoid the decompose caused by the temperature, we first tested all the molecules and the substrate within a range of temperature with the same ReaxFF force filed which will be used as the pair coefficient in the simulation. Figure 5 shows the possible models that will be used in our simulation. First is the test of each components in the simulation, and then the first cycle of ALD simulated with the H₂O or OH molecules added, then the second cycle, TMA added to the system, and finally we also increase the temperature to observe the temperature of this ALD system.

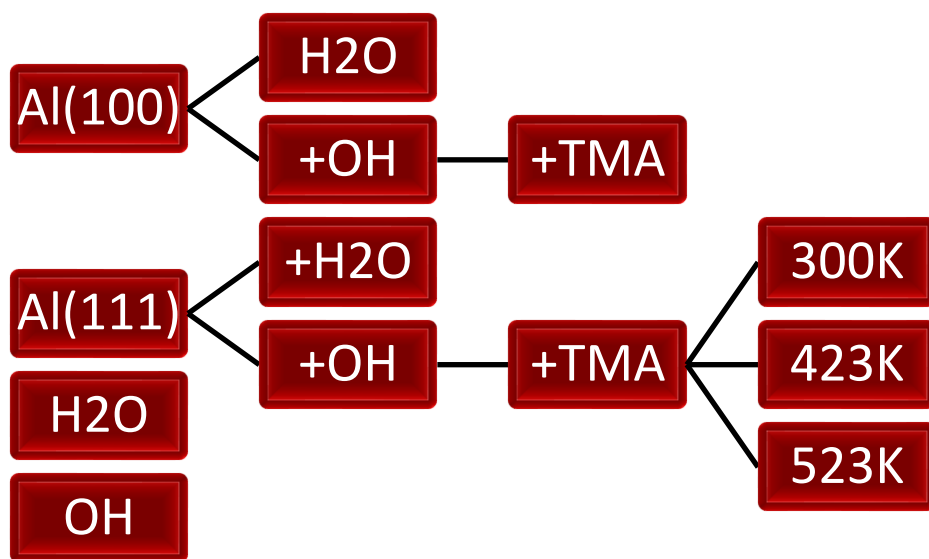


Figure 5. Simulation models.

In order to make the chemical reactions occur smoothly, the time step needs to be lower than 1 order of the highest frequency of molecules, which is usually at 0.5 to 1.0 fs. The time step of the interaction in this work is 0.25fs and we performed the simulations for at least 0.5ps which is 2000 iterations and the longest time is 250ps which is 1000,000 iterations. The temperature is also an essential fact needed to be well controlled, so a canonical ensemble, with constant particles, constant volume, and constant temperature has been performed in the

simulation in LAMMPS. The ReaxFF code is in Appendix A and the whole input for LAMMPS is put in Appendix C.

ADF Simulation

In the ADF simulation, unlike that in the LAMMPS which all the input atom position must be prepared separately, the procedures can be done in only one window. Here is the procedure to create the model for this work by ADFjobs.

1. Create a new input file with ADFjobs and switch to ReaxFF mode from the option at the panel bar “ADF → ReaxFF”.
2. Creating the surface by first creating bulk aluminum which has an fcc crystal structure, with a lattice constant of about 4.0 Angstrom. An aluminum atom is first added by using “Edit → Crystal → Cubic → fcc”, and in the dialog that appears, select the preset Al.
3. Create a slab by “Edit → Crystal → Generate Slab...” and here we can design the number of layers of the aluminum slab. Then in the dialog window, check the “Cartesian” check box and set the number of layers here. Apart from this, the orientation or Miller indices of the substrate is also defined here. We mainly created and studied Al(100) and Al(111) substrate.
4. In this work we do not want just one unit cell, but a much bigger piece of the slab. We can create the supercell by “Edit → Crystal → Generate Super Cell...”. The size of the model or the number of atoms of the substrate is defined in the dialog that follows.
5. The next step is to add the precursors, water or the hydroxide, to the system. There are two ways to add the precursors. The molecules can be created manually or automatically by the builder from “Edit → Builder”.

6. In the dialog, we can change the dimension of the lattice vectors to change the shape and scale of the simulation box. The species of the molecules we add can be decided from the last box after “Fill box with” and some of the molecules such as water and oxygen can be found in the file of SCM downloaded with the software, but some others such as TMA, need to be prepared in advance as .xyz file. The number of molecules should be specified in the box right after the “Fill box with”. If there are more than one types of molecules, we can add species by the “+” in front of “Molecules”.
7. We can specify a distance between the molecules by Angstrom. Click the “Generate Molecules” button to generate molecules.
8. Now we will set up the MD-simulation. We will use the AlCHO force field and a Nose-Hoover thermostat with a default damping constant of 100 fs. All these settings are in the panel bar “Main”.
9. The temperature can be controlled by a temperature regime, specifying different temperatures for different regions (panel bar “Model → Regions”). From this, we can define different temperature in different parts of the model. For example, we can define two regions: one for the aluminum slab, and one for the water, so that we can use a high temperature for water but try to keep the aluminum cool at the same time.
10. After all the regions we needed have defined, we will set up the temperature regime on the panel bar “Model → Temperature Regime”. The Temperature Regime can also be used to change the temperature such as heating and cooling.
11. The last step is to save the file and run it by “File → Run”.
12. The movie of the simulation result and other results such as energy and species can be seen in the movie (“SCM → Movie”).

In the ADF simulation, we do the simulation with a module of 300 or 1000 Al atoms in the substrate and 1000 OH/H₂O molecules as the precursor under the temperature of 300K, 473K and 573K separately. The ReaxFF code we use the Al/C/H/O code implemented in the Jan 2016 version. We choose to use the Nose/Hoover thermostat with a temperature damping constant of 100 fs and a time step of 0.25 fs and run the simulation for ~ 10000 iteration.

RESULTS AND DISCUSSION

Validation of the ReaxFF Force Field for Each Component

As it is discussed above, the minimization results of the molecules show that the distance between oxygen and hydrogen atoms in the water molecules is around 0.94 Å and the angle is 101.9 degrees, which is a little bit less than the normal value, 0.96 Å and 104.5 degrees. The distance between oxygen and hydrogen atoms in the hydroxide ions is 0.91 Å, also smaller than 0.96 Å. These results indicate that the bond between the oxygen and hydrogen atoms may be a little bit stronger than that as usual.

To study the mechanism of the precursors interacting with the Al substrate and find out the temperature dependence, it is necessary to test the substrate and the precursors separately

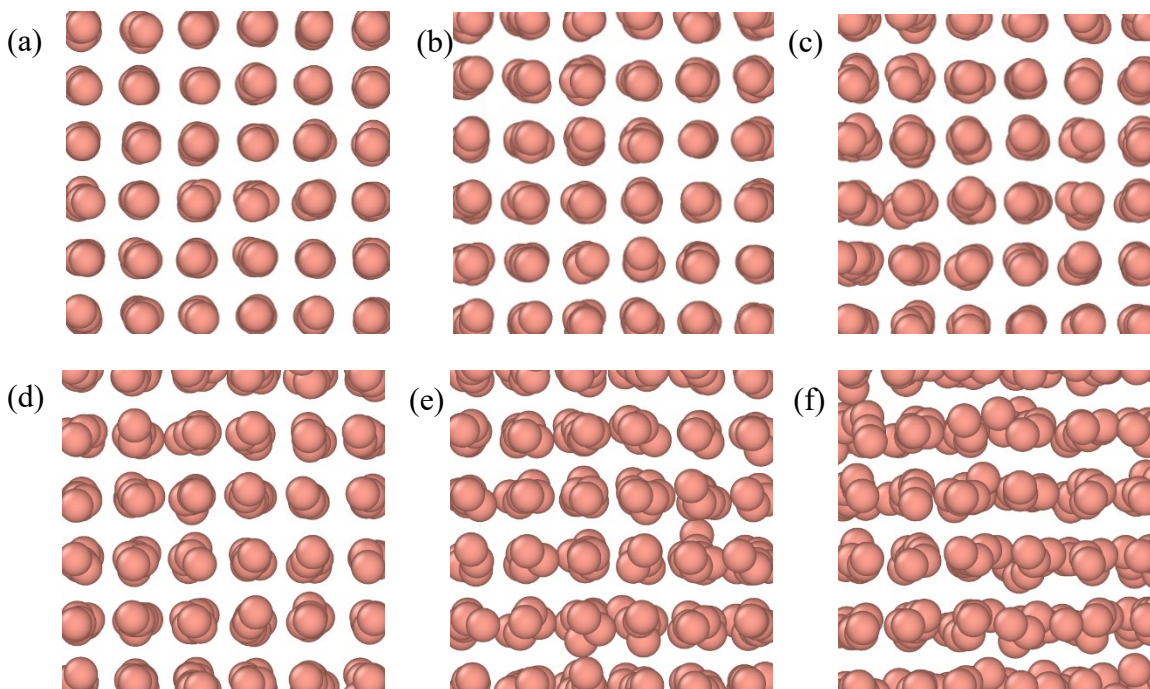


Figure 6. Al(100) substrate under the temperature of (a) 300 K, (b) 423 K, (c) 523 K, (d) 623 K (e) 723 K and (f) 823 K.

under the ReaxFF force field first to make sure they do not melt or decompose within the temperature range we simulate.

We first heat the substrate with an increasing temperature from room temperature (300K) to up to 2000 K. Figure 6 shows the lattice of the Al(100) substrate and the stability of it under different temperature before the melting temperature (933.473 K) in the reference mentioned above. According to the figures, the structure of the substrate with the orientation (100) become more and more unstable with the increasing temperature. The substrate is relatively stable below 723 K, and it becomes disorder above 723 K.

However, there is still a little bit difference between the result of Al(100) and Al(111). In these figures in figure 7, the Al(111) structure shows a better stability at all temperature we tested, which means it is expected to have a better stability in the ALD simulation after the

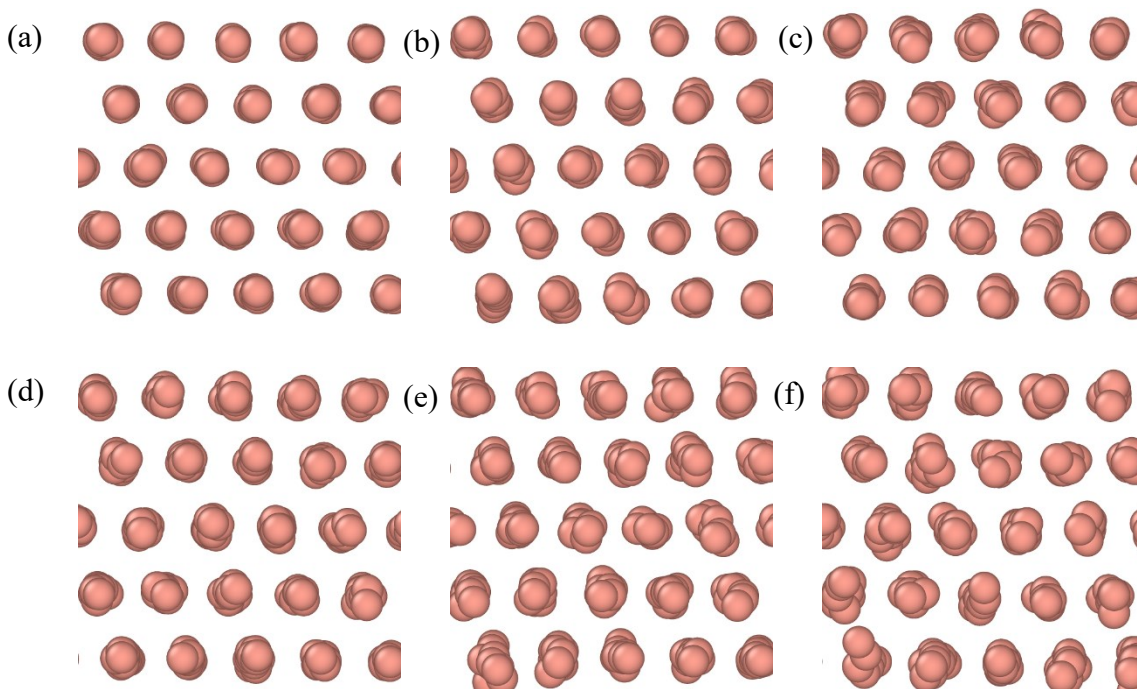


Figure 7. Al(111) substrate under the temperature of (a) 300 K, (b) 423 K, (c) 523 K, (d) 623 K (e) 723 K and (f) 823 K.

precursors are added into the system, and the substrate would be a better choice for controlling the interactions to get the ultrathin layer.

In the ALD process, it is necessary to keep the substrate stable and do not melt. Therefore, in the simulation that follows we control the temperature no more than 623 K to make sure the whole structure is stable.

Figure 8 shows the interactions between the water molecules at 300 K after 20000 iterations (5 ps) as well as that of the hydroxide. It can be easily seen that both H_2O and OH

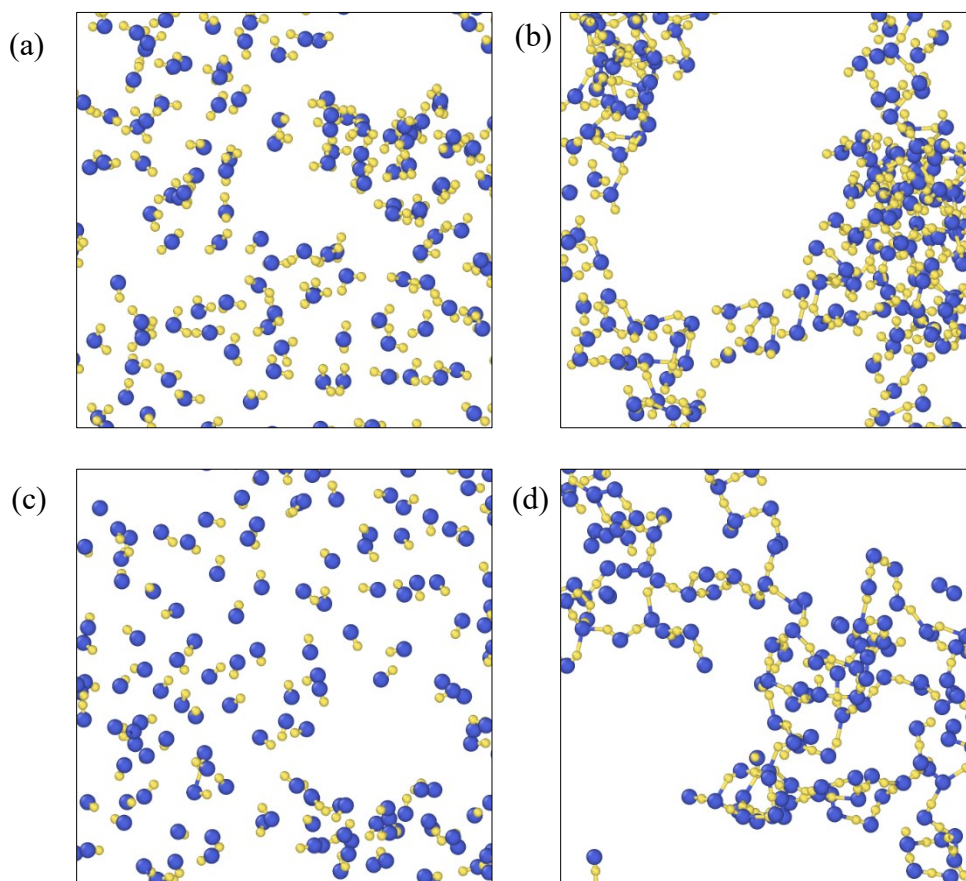


Figure 8. H_2O (a) before the simulation and (b) after the simulation at 300 K; and OH (c) before the simulation and (d) after the simulation at 300 K.

would become cluster when there are no other molecules existing in the system. It is because of the hydrogen bonds between the oxygen and the hydrogen atoms.

In other worlds, the density of the molecules (0.0003g/cm^3) is far more less than the density of water, so there will be hydrogen bonds between water molecules and finally the liquid forms. However, the water molecules are almost stable during the simulation while some of the hydroxide may dissociate and few oxygen molecules forms during the simulation because the structure of OH is not stable and the H_2O structure is the most stable structure between oxygen and hydrogen

Figure 9, the figure of the Radial Distribution Function of H_2O describes how density varies as a function of distance from the hydrogen and oxygen atom.

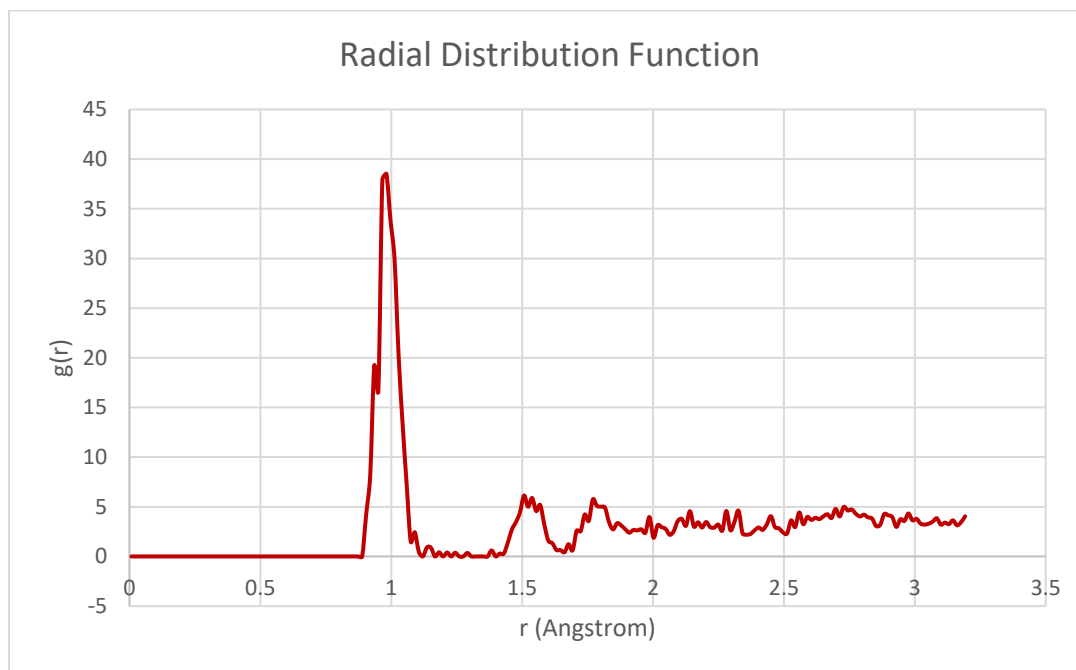


Figure 9. Radial Distribution Function of H_2O .

The first peak which is shown at around 0.9 Å is the peak of the bonds between the oxygen and hydrogen within a water molecule, and the second peak, the one at around 1.5 Å is the hydrogen bonds between the molecules.

Apart from the Al substrate and H₂O/OH, TMA is also tested. Figure 10 illustrates the interactions between the TMA molecules in the temperature range that will be study. TMA molecules are really stable and do not become chains or clusters as the water or hydroxide.

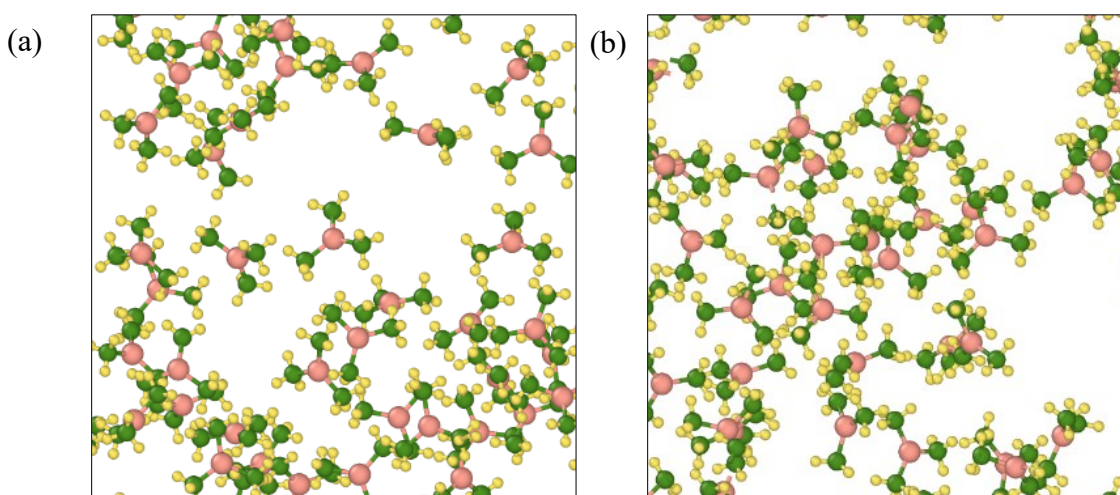


Figure 10. TMA (a)before the simulation and (b) after the simulation at 300 K.

According to all the tests above, the components are all stable under the temperature 300K to 623K, which means if there is any interaction in the simulation that follows, it may not just because of the change of the temperature, but would due to the other existing molecules so it can help us analyze the mechanism of the interactions.

The Effects of Substrate Orientation and the Type of Precursors

According to the ALD process, the H_2O or OH precursor need to be first put above the Al substrate. We first randomly put 18 H_2O molecules above the Al(100) and Al(111) substrate separately and run the simulation for 5 ps.

The Ability of Adsorption of Al(100) and Al(111). Here we first discuss the ability of adsorption of the substrate of different orientation.

In both modules, the temperature is set at 300K as it is shown in figure 12 and 13, and the real temperature of the system is first increase and then reach 300K after about 3000 steps, and the temperature will be waving around 300K. In both modules the H_2O molecules have successfully adsorbed on the surface of the substrate which can be seen from figure 11.

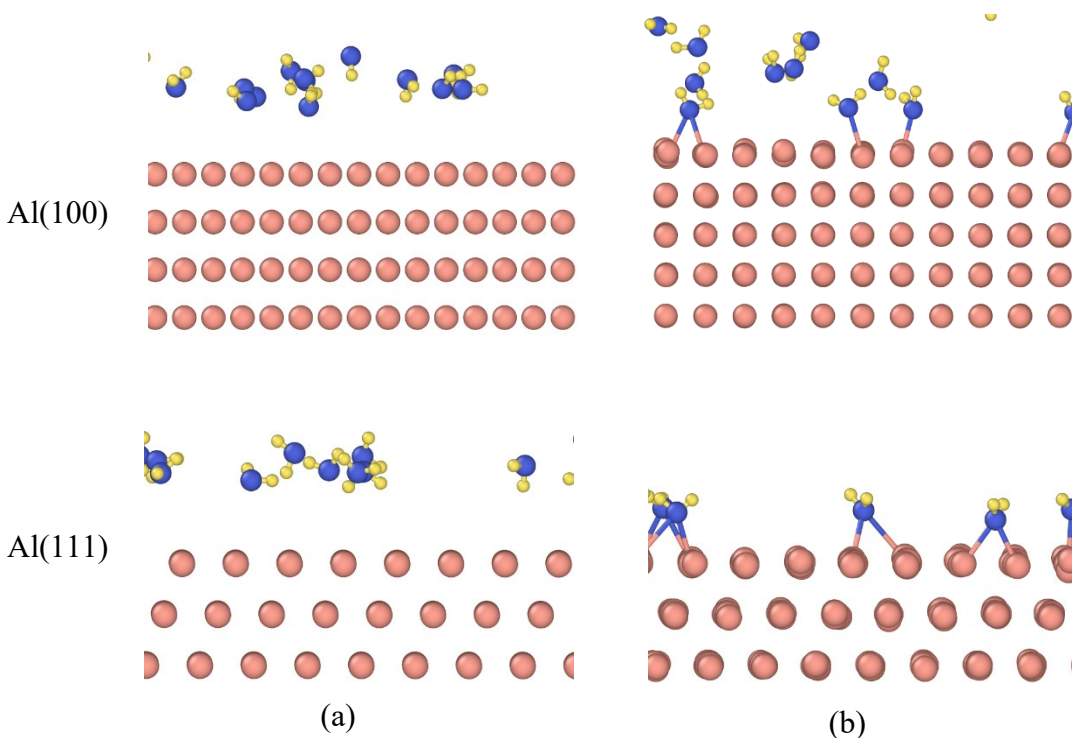


Figure 11. H_2O (a) before the simulation and (b) adsorbed on Al substrate at 300 K after 5ps.

And after the adsorption most of the water molecules caught by Al(111) substrate will move around on the surface and will not leave the surface while on the Al(100) substrate, some

of the molecules would leave after a while. In this case, in our study, there are more water molecules adsorbed on Al(111) substrate than that on Al(100)

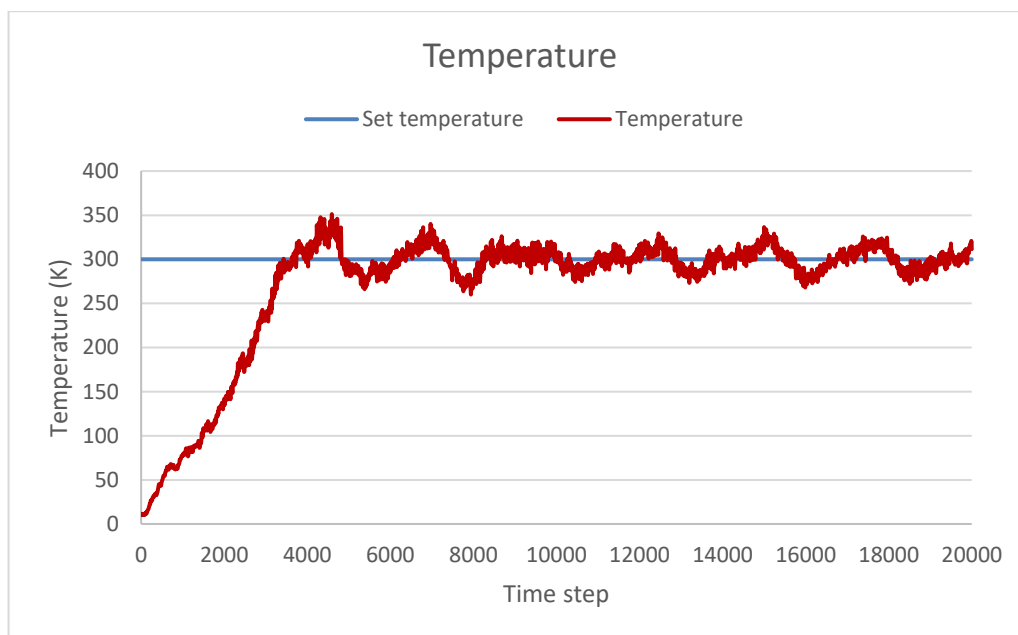


Figure12. The temperature change during the simulation for Al(100) + H₂O.

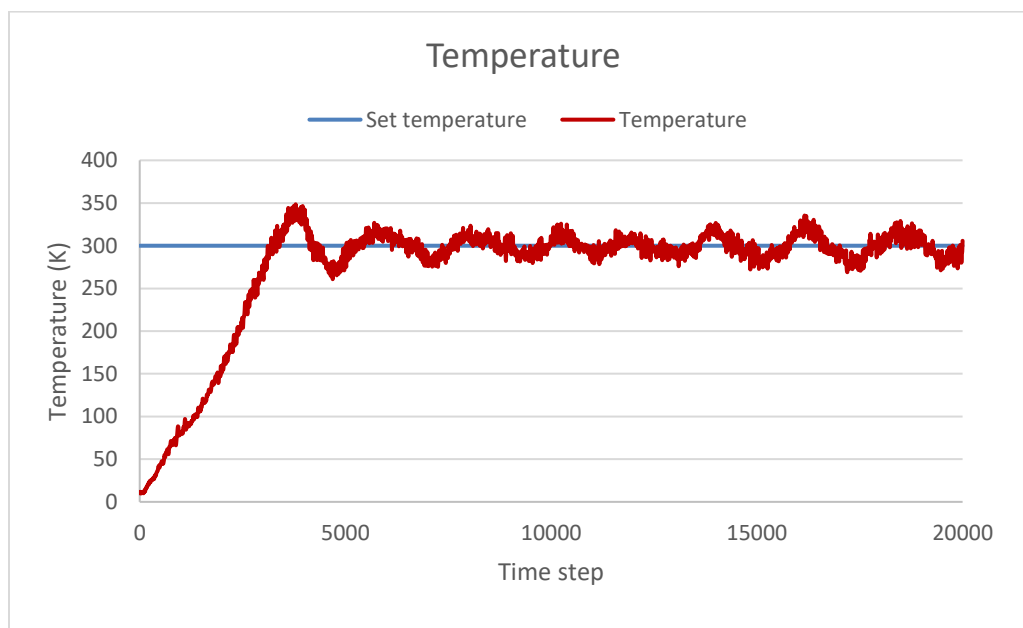


Figure 13. The temperature change during the simulation for Al(111) + H₂O.

substrate. However, we did not see the dissociation of the water molecules and the interactions between the molecules which means that the water molecules are quite stable on the substrate and the bonds between oxygen and hydrogen is strong under this ReaxFF force field.

We also tested the OH precursor on both Al(100) and Al(111) substrate. Figure 14 shows the interactions between OH and aluminum substrate at 300 K.

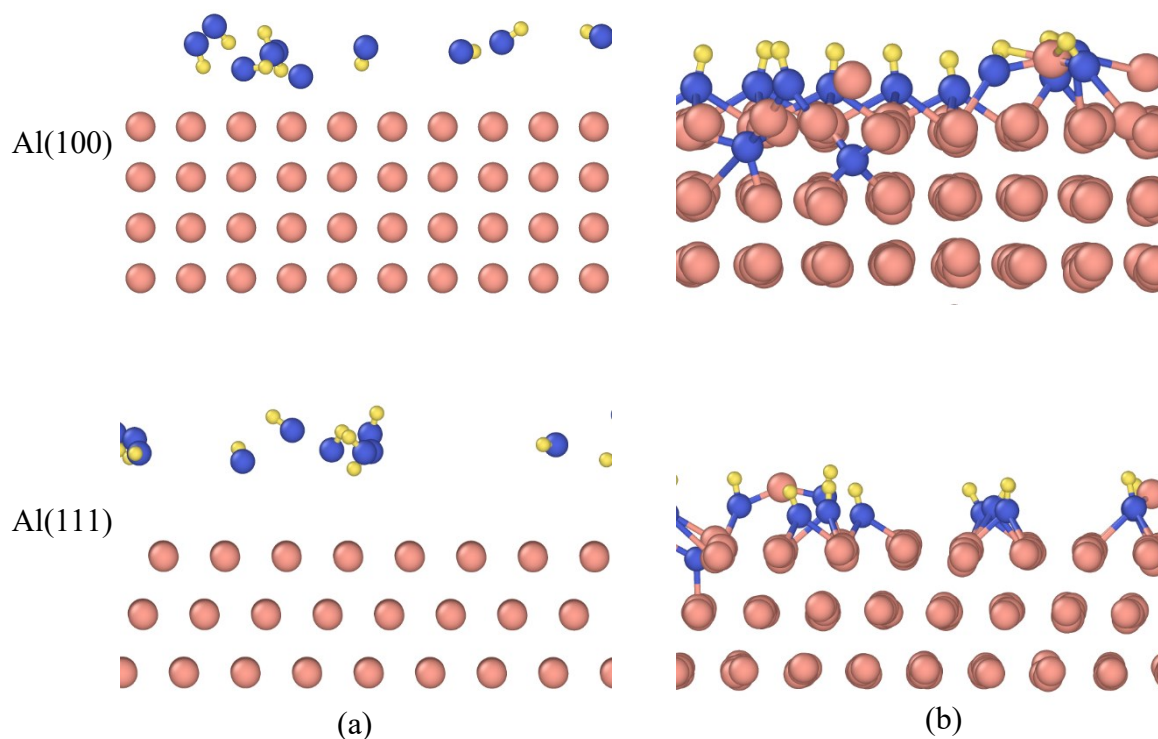


Figure 14. OH (a) before the simulation and (b) adsorbed on Al substrate at 300 K after 5ps.

According to the figures, most of the OH have been adsorbed by the substrate and it shows that there is nearly no obvious difference in the ability of adsorbing OH ions between the two substrates, which may due to the active property of the OH ion itself. Figure 15 and 16 shows the simulation temperature is relatively stable at 300K.

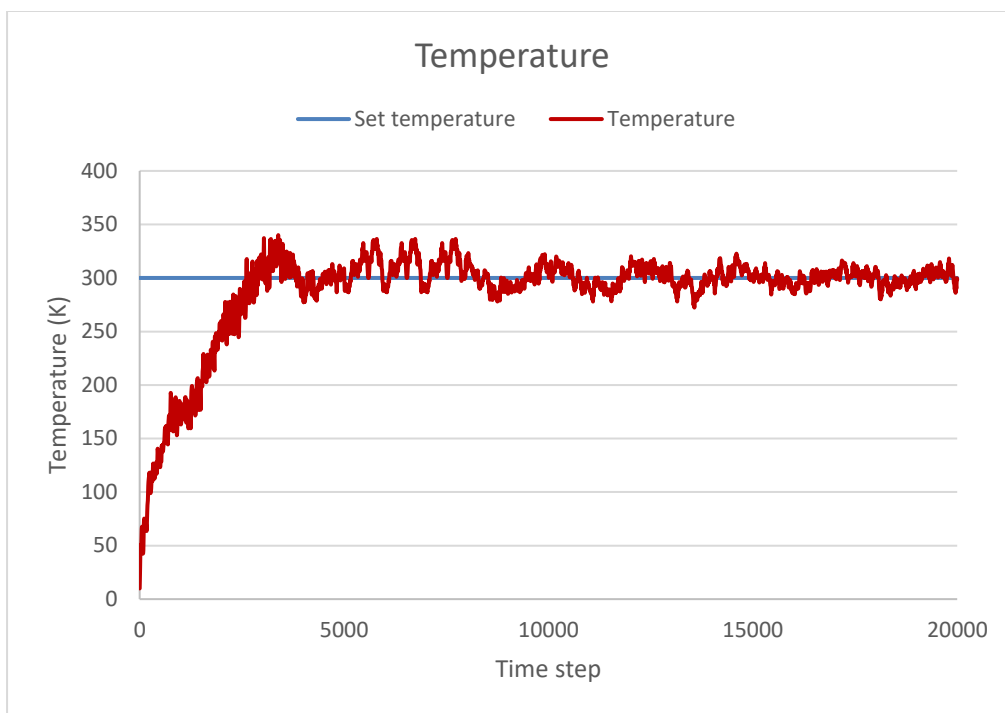


Figure15. The temperature change during the simulation for Al(100) + OH.

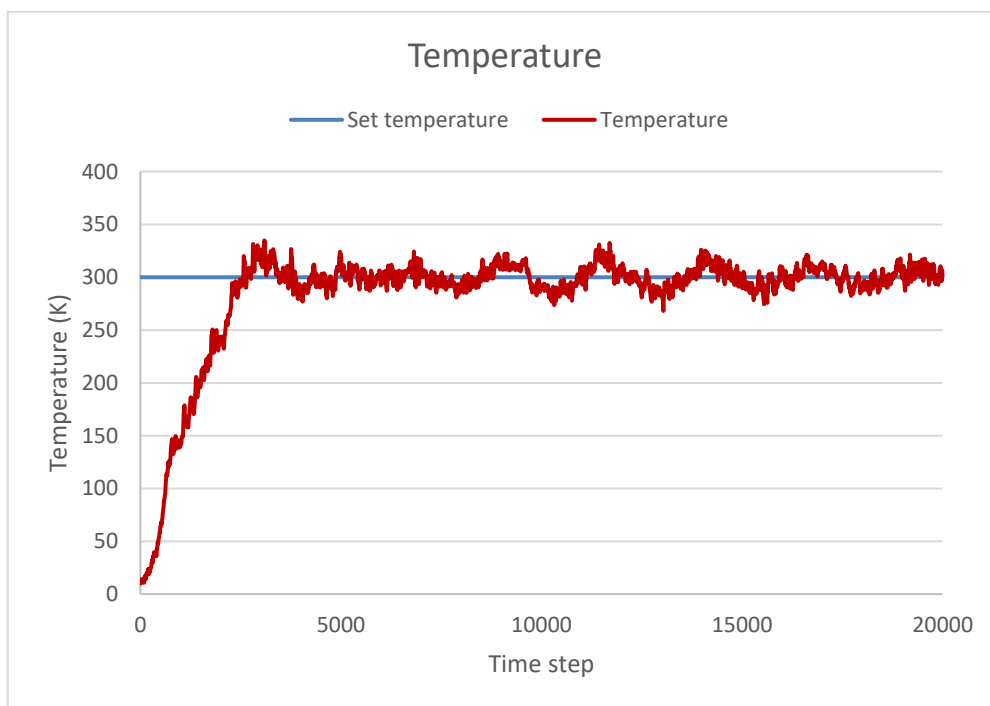


Figure 16. The temperature change during the simulation for Al(111) + OH.

The reason that Al(111) would absorb more water molecules may be due to the surface density of the Al(111) is much higher than that of Al(100), because the Al substrate in ALD is to create dense H₂O/OH layer for the interactions that follow.

The Adsorption of H₂O and OH Precursors. Comparing the adsorption ability of the two kinds of precursors, H₂O and OH from figure 11 and 14, it is obvious that Both Al(100) and Al(111) substrate have better ability adsorbing OH than H₂O, and after the adsorption of OH, most of the OH will still be on the surface and tend to stay in the middle of the “hole” among the aluminum atoms on the surface as that in figure 17. And few of the OH ions will dissociation as shown in figure 17 where the hydrogen goes away, and the oxygen will further be pulled into the aluminum.

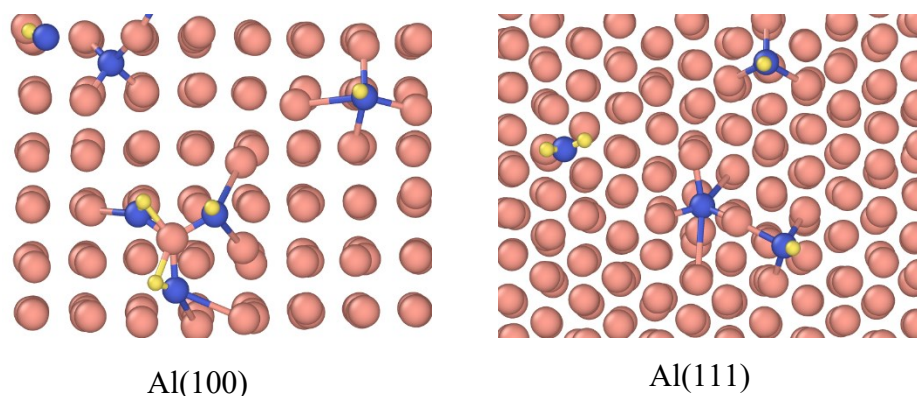


Figure 17. OH adsorbed on Al(100) and Al(111) substrate at 300 K 5ps from z-direction.

In this case, the hydrogen atoms may be adsorbed by an oxygen atom in OH and become a water molecule. It indicates that after the adsorption and dissociation of OH on the Al substrate, the oxygen atoms would diffuse inward the substrate. Another obvious phenomenon which shown in figure 14 is that when an aluminum atom is right in the middle of two OH ions,

it may possibly be pulled out from the substrate. This will lead to the dissociation or unstable of the substrate when there are a large amount or high density of OH existing on the surface.

Temperature Dependence

The result of the temperature dependence shows in figure 18, simulating at 300 K, 373 K, 473 K and 573 K separately. H_2O shows better stability in the simulation and would not make the substrate so unstable as that of OH, so we increase the temperature in the simulation and increase the scale of the module to see if the water would dissociate into OH and H which will be better interacting with TMA in the next step at a higher temperature.

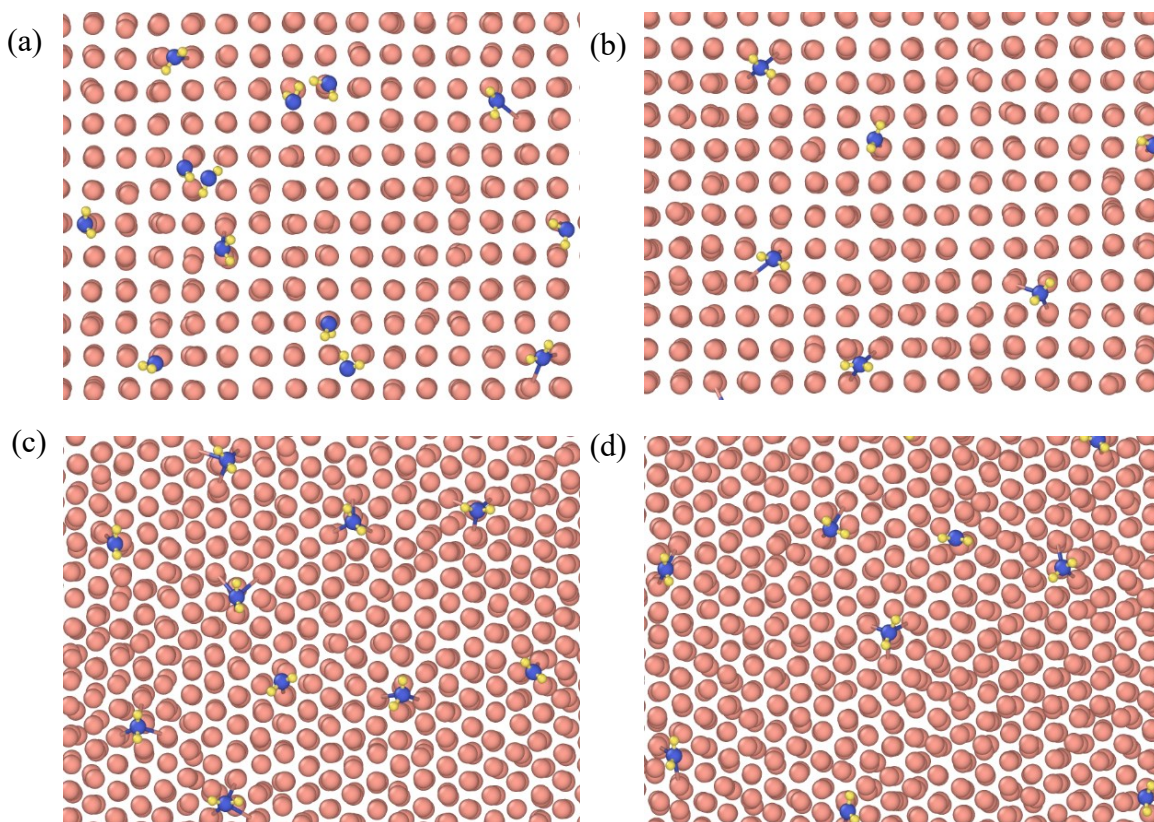


Figure 18. H_2O adsorbed on Al(111) substrate at (a) 300 K (b) 373 K, (c) 473 K and (d) 573 K.

In this module, there are 331776 aluminum atoms as well as 4608 water molecules. With such a large scale which cannot be processed by QM systems, ReaxFF shows its advantage, larger samples would lead to more accuracy.

From the figures, we can see that after the water molecules adsorbed by the substrate, they do not dissociate as we expected, while the substrate tends to be unstable quicker than the H_2O molecules. Although the temperature is raised to 573K, it shows no even a single H_2O molecule dissociate, which means it would be quite difficult for TMA to adsorb on the oxygen in these modules. Figure 19, 20 and 21 shows the interactions between OH and TMA in details.

Interactions Between OH and TMA

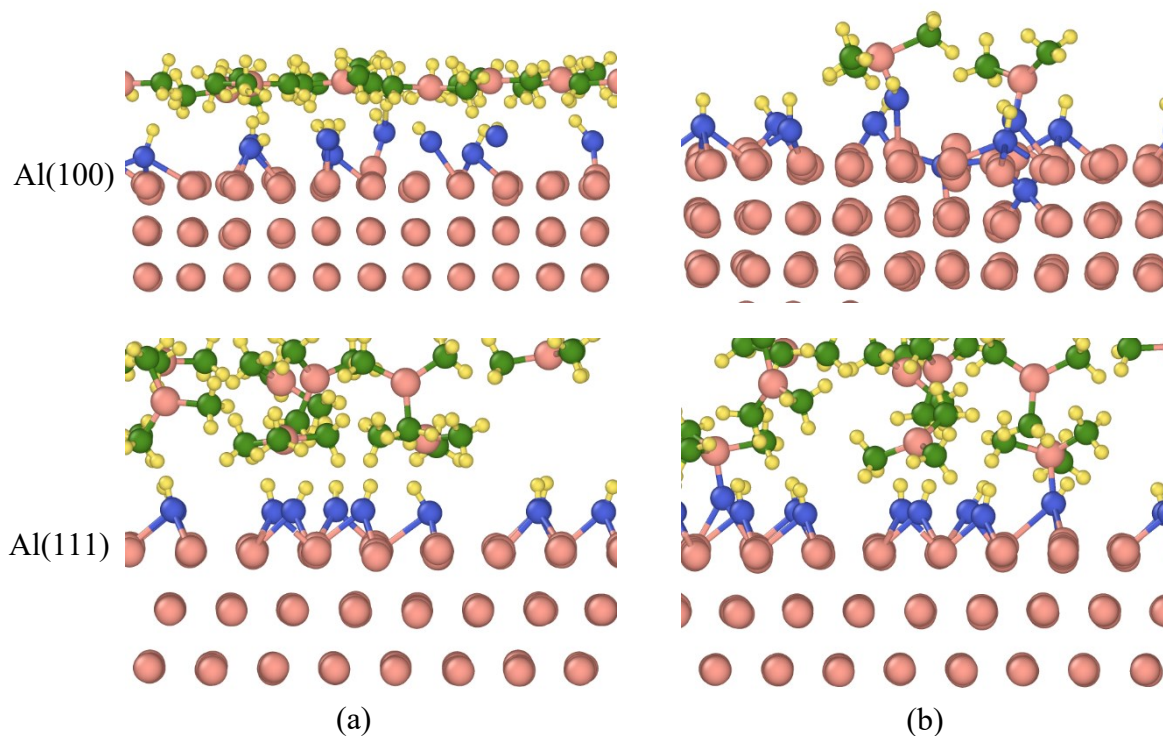


Figure 19. TMA adsorbed on OH precursors on (a) Al(100) substrate and (b) Al(111) substrate at 300K.

The next step after adding the H₂O or OH precursors is to add TMA above the H₂O or OH layer and it is expected that the aluminum atom of the TMA would adsorb by the oxygen atom in the OH which adsorbed by the substrate.

The Adsorption of TMA on the Al(100) and Al(111) Substrate. Because there are three methyl around the aluminum atom in a TMA molecule which already increase the difficulty to observe the interactions between oxygen and aluminum, we only simulate the interaction between OH and TMA rather than H₂O.

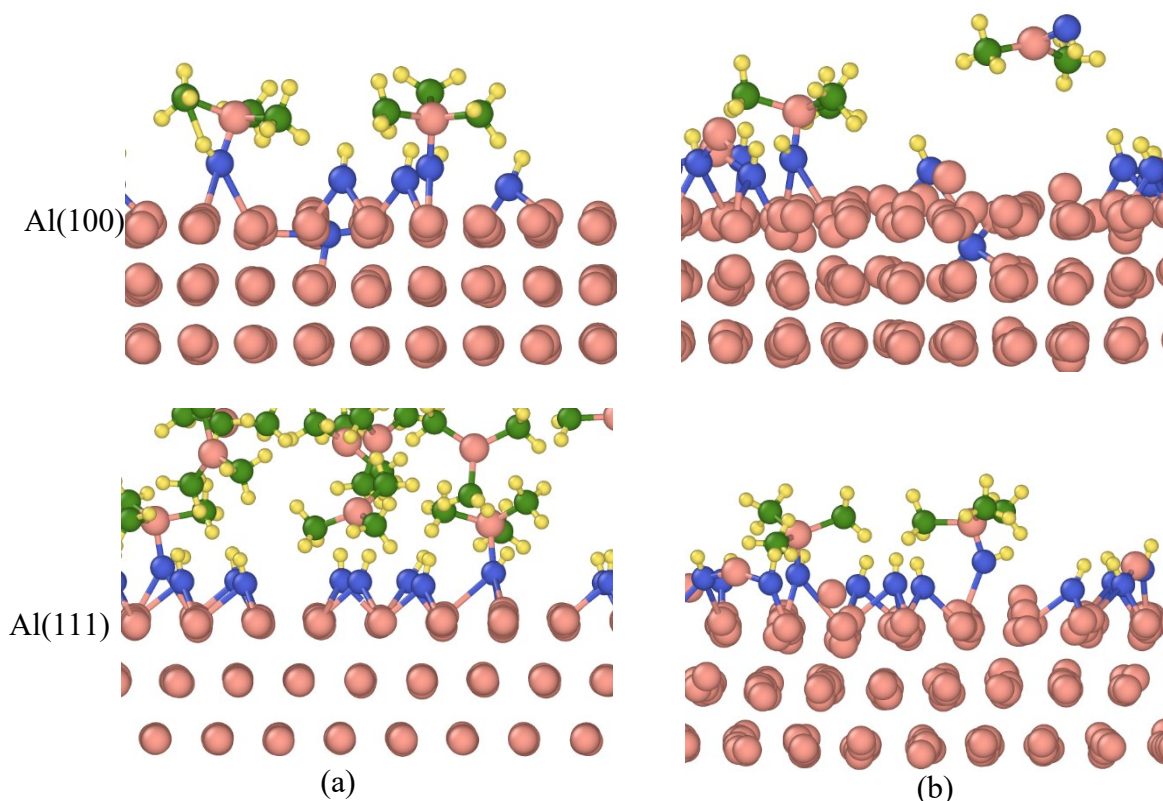


Figure 20. TMA adsorbed on OH precursors on Al substrate at (a) 300 K and (b) 623 K.

Unlike the H₂O or OH which can be easily adsorbed by the substrate, it is more difficult for a TMA molecule to be adsorbed by the oxygen because there are three methyl around the aluminum atom and the methyl is repulsive with the aluminum substrate. In this case, the TMA

must be in a suitable position and be close enough so that the aluminum would have the chance to be adsorbed by the oxygen. Figure 18 shows the result of the simulation. The TMA molecules can successfully be adsorbed by the OH on both Al(100) and Al(111) substrate.

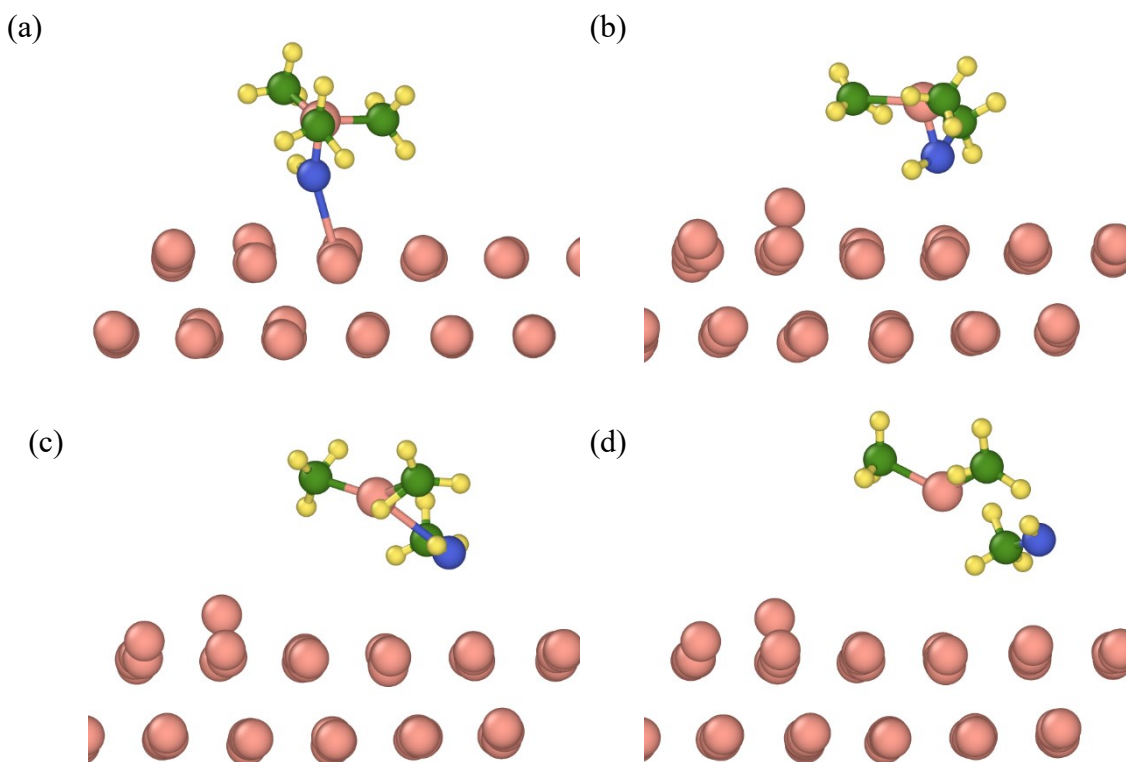


Figure 21. Interaction procedure between TMA and OH at 573K 100 fs.

From figure 19 and 20, it is obvious that the Al(111) substrate have better stability in the reaction. With the temperature increases, the TMA molecules tend to dissociate, and if they are adsorbed by the OH, it is possible that the OH be pulled out from the substrate which is shown in figure 21 and figure 22. A dimethylaluminum (DMA) is formed as well as a CH_3OH at 573K.

It is obvious that at the temperature 573K from figure 21, after the TMA interact with OH, the OH is been pulled out from the Al substrate. After that, the OH interacts with one of the methal and than the bond between Al and O breaks, forming a DMA and an methenol molecule.

However, in figure 22, after the hydrogen of OH taken by the methal of the TMA, the whole TMA flies out from the OH, and finally breaks into a DMA and a methane.

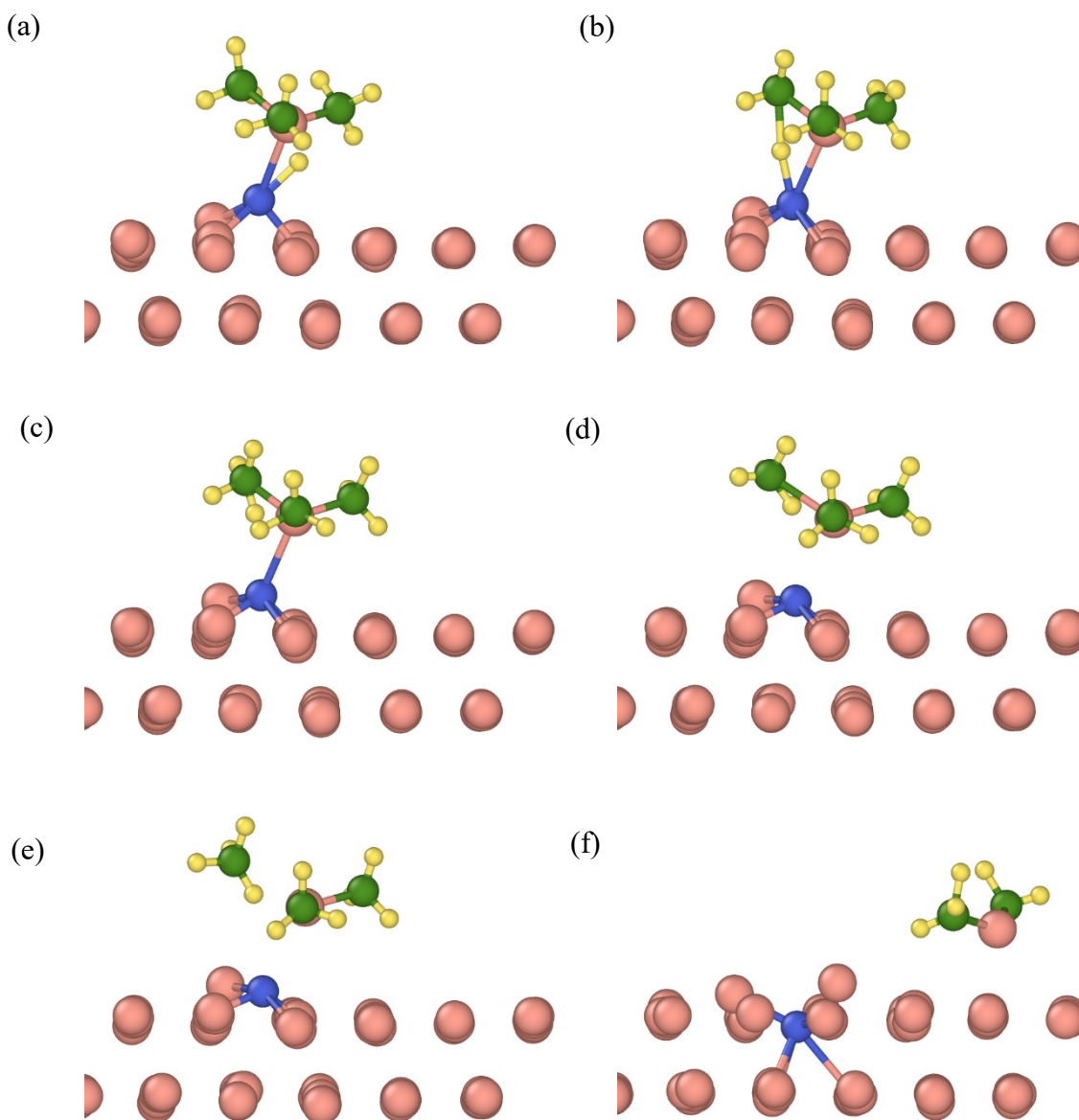


Figure 22. Interaction between TMA and OH at 673K.

However, according to the ALD process, what we would like to see is the adsorption of the Al atom in TMA with the oxygen atom in OH, and the methane forms and goes out. If the Al

does not been adsorbed, it will not be a successful trial. So, increasing the temperature will help dissociating the TMA, but may also lead to the bond breakage between Al and O atoms.

Simulations Results With ADF

ADF is a convenient software that we can easier create the module and write the input information. It has a convenient interactive window where most command in the LAMMPS can be found correspondingly. The result that shows the interaction between water and the substrate is shown in the figure 23 below.

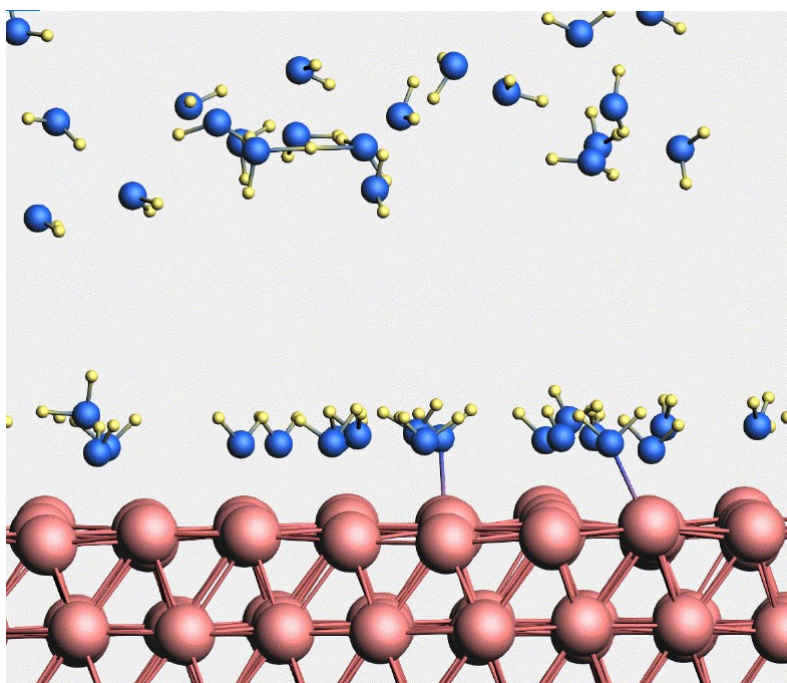


Figure 23. The simulation results by ADF.

Limitations of ReaxFF

The ReaxFF force field is very good and convenient for MD simulation and for the ALD process because it contains much information to describe the interactions between particles and it

can manipulate the model of a large size as well as large time scale. These advantages can help better observe the interactions of the particles.

However, for this simulation, including a large aluminum substrate including thousands of atoms, there are still some limitation that we mentioned above. The first one is with the aluminum substrate. The aluminum substrate begins to melt at around 723K under the melting point (~933K). The second one is with the water precursor; H₂O molecules still gather as liquid above the boiling point (373K) and still have strong hydrogen bonds at 623K as shown in figure 24 below.

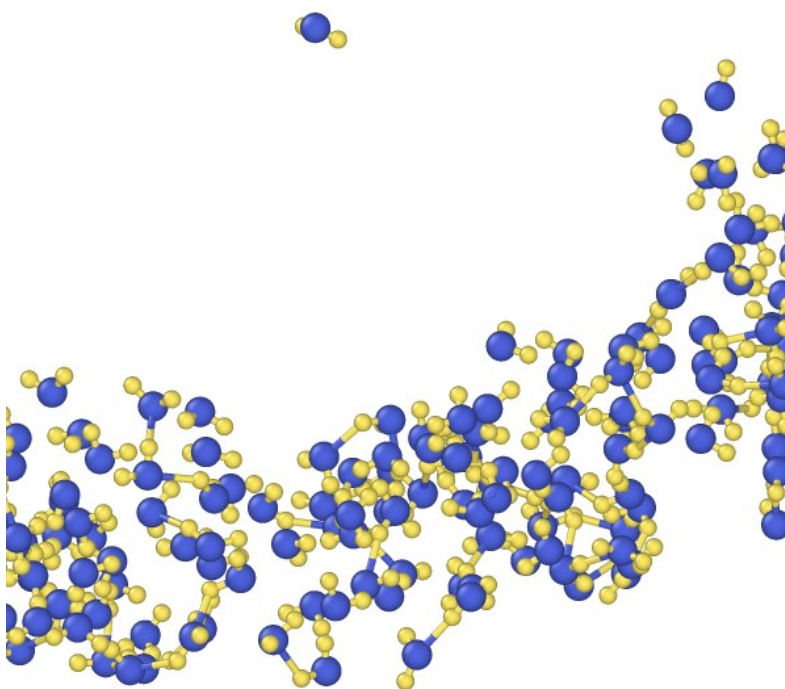


Figure 24. Water molecules simulating at 623K.

The pair interactions can be seen in table 1, which may help explain the possible reason why aluminum is unstable below the melting point.

Table 1. List of pair interactions.

Number of bonds	Number of off-diagonal terms	Number of angles	Number of torsions	Number of hydrogen bonds
C-C	C-H	C-C-C	C-C-C-C	O-H-O
C-H	C-O	C-C-H	C-C-C-H	
H-H	H-O	H-C-H	H-C-C-H	
C-O	C-Al	C-C-O	C-C-C-O	
H-O	H-Al	H-C-O	H-C-C-O	
O-O	O-Al	O-C-O	O-C-C-O	
C-Al		C-H-C	C-C-O-C	
H-Al		C-H-H	C-C-O-H	
O-Al		C-H-O	H-C-O-C	
Al-Al		H-H-H	H-C-O-H	
		H-H-O	H-C-O-O	
		O-H-O	O-C-O-C	
		C-O-O	O-C-O-H	
		C-O-C	C-O-O-H	
		C-O-H	H-O-O-H	
		H-O-H	C-O-O-O	
		H-O-O	H-O-O-O	
		O-O-O	O-O-O-O	
		C-O-Al	X-C-H-X	
		H-O-Al	X-H-H-X	
		O-O-Al	X-H-O-X	
		Al-O-Al	X-O-O-X	
		O-Al-O	X-C-C-X	
		O-Al-Al	C-C-O-O	
		C-Al-C	C-O-O-C	
		Al-C-Al	O-C-O-O	
		H-C-Al		
		C-Al-O		
		C-C-Al		
		C-Al-Al		
		H-Al-H		
		H-Al-Al		
		H-Al-Al		
		Al-H-Al		
		H-H-Al		
		C-Al-H		
		C-H-Al		

The first limitation may be due to insufficient description of 3-body and 4-body interactions including aluminum. In the ReaxFF file, there are lists of interactions and the parameters that needed written as shown in appendix A.

However, there is no information about 3-body interactions of Al-Al-Al and 4-body interactions about aluminum as the pair interactions are shown in table 1, while it is existing in the Al substrate. Without that information, the substrate would be weaker than it should be and be more unstable.

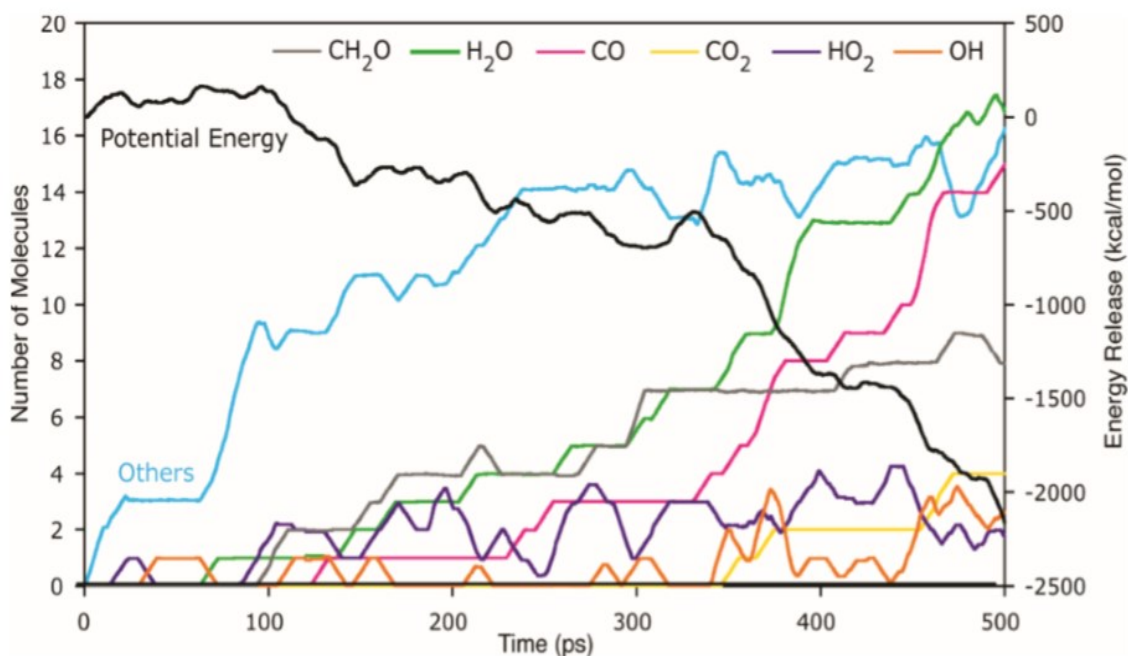


Figure 25. Product distribution observed at 500 ps for the NVT-MD simulation of a mixture of hydrocarbons in an O₂ atmosphere. Only major products are shown explicitly; all intermediates and minor products are included as “others”.¹⁴

The second limitation about the water molecules may be due to the insufficient description of the interactions between hydrogen and oxygen in the process getting the parameter. Figure 24 shows the interaction getting the parameters. It is in a system that

hydrocarbon interacting with oxygen molecules, and the water is only one of the minor products (up to 4 molecules). This may be the main reason behind the limitation in applying the existing ReaxFF potential for denser water system like the one in this study.

SUMMARY

Overall, reactive MD simulations using ReaxFF were able to capture key chemical reactions of ALD process, and the key adsorption mechanisms can be observed in our study, which shows that the existing ReaxFF potential is useful in the simulation of the ALD process with a large scale model and a long time scale.

In the simulation, the ALD components such as aluminum, H_2O , OH and TMA are found to be stable during the simulation and their basic properties and interactions within the atoms can be also expressed using ReaxFF potential.

When looking more insight into the ALD processes, the Al(111) structure shows a better stability at all temperature we tested, which means it is expected to have a better stability in the ALD simulation after the precursors are added into the system, and the substrate would be a better choice for controlling the interactions to get the ultrathin layer. Both H_2O and OH molecules are successfully adsorbed by the substrate, and both Al(100) and Al(111) substrate have better ability adsorbing OH than H_2O . The H_2O molecules are really stable on the substrate even the temperature raised to 623K, the highest temperature that the substrate can be stable. However, OH produces inward the oxygen diffusion on the substrate after dissociation. After TMA molecules added, the interaction of TMA and OH is also observed. With the temperature increase, the TMA tend to dissociate and pull the OH from the substrate.

The ReaxFF force field is a good method for ALD simulation with much convenience and accuracy, but it has some limitations due to insufficient description of 3-body and 4-body interactions including aluminum and the limited applications toward denser water systems.

Future development of ReaxFF for ALD process will need to include the TMA and water pulses as a part of optimization of the parameters.

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APPENDICES

Appendix A. Reaxff File ¹⁴

ReaxFF force field

Reactive MD-force field: Al/C/H/O JPCC Jan. 2016

39 ! Number of general parameters
50.0000 !Overcoordination parameter
9.5469 !Overcoordination parameter
26.5405 !Valency angle conjugation parameter
1.7224 !Triple bond stabilisation parameter
6.8702 !Triple bond stabilisation parameter
60.4850 !C2-correction
1.0588 !Undercoordination parameter
4.6000 !Triple bond stabilisation parameter
12.1176 !Undercoordination parameter
13.3056 !Undercoordination parameter
-70.5044 !Triple bond stabilization energy
0.0000 !Lower Taper-radius
10.0000 !Upper Taper-radius
2.8793 !Not used
33.8667 !Valency undercoordination
6.0891 !Valency angle/lone pair parameter
1.0563 !Valency angle

2.0384 !Valency angle parameter
6.1431 !Not used
6.9290 !Double bond/angle parameter
0.3989 !Double bond/angle parameter: overcoord
3.9954 !Double bond/angle parameter: overcoord
-2.4837 !Not used
5.7796 !Torsion/BO parameter
10.0000 !Torsion overcoordination
1.9487 !Torsion overcoordination
-1.2327 !Conjugation 0 (not used)
2.1645 !Conjugation
1.5591 !vdWaals shielding
0.1000 !Cutoff for bond order (*100)
2.1365 !Valency angle conjugation parameter
0.6991 !Overcoordination parameter
50.0000 !Overcoordination parameter
1.8512 !Valency/lone pair parameter
0.5000 !Not used
20.0000 !Not used
5.0000 !Molecular energy (not used)
0.0000 !Molecular energy (not used)
2.6962 !Valency angle conjugation parameter

C 1.3825 4.0000 12.0000 1.9133 0.1853 0.9000 1.1359 4.0000
 9.7602 2.1346 4.0000 33.2433 79.5548 5.8678 7.0000 0.0000
 1.2104 0.0000 199.0303 8.6991 34.7289 13.3894 0.8563 0.0000
 -2.8983 2.5000 1.0564 4.0000 2.9663 0.0000 0.0000 0.0000
 H 0.7853 1.0000 1.0080 1.5904 0.0419 1.0206 -0.1000 1.0000
 9.3557 5.0518 1.0000 0.0000 121.1250 5.3200 7.4366 1.0000
 -0.1000 0.0000 62.4879 1.9771 3.3517 0.7571 1.0698 0.0000
 -15.7683 2.1488 1.0338 1.0000 2.8793 0.0000 0.0000 0.0000
 O 1.2477 2.0000 15.9990 1.9236 0.0904 1.0503 1.0863 6.0000
 10.2127 7.7719 4.0000 36.9573 116.0768 8.5000 8.9989 2.0000
 0.9088 1.0003 60.8726 20.4140 3.3754 0.2702 0.9745 0.0000
 -3.6141 2.7025 1.0493 4.0000 2.9225 0.0000 0.0000 0.0000
 Al 2.4443 3.0000 26.9820 2.0089 0.2161 0.5675 -1.6836 3.0000
 11.8538 16.3962 3.0000 0.0076 16.5151 -0.2451 6.3319 0.0000
 -1.0000 0.0000 67.5458 137.9671 0.2042 0.0000 0.8563 0.0000
 -14.9162 3.0000 1.0338 3.0000 2.5791 0.0000 0.0000 0.0000
 10 ! Nr of bonds;
 Edis1;LPpen;n.u.;pbe1;pbo5;13corr;pbo6;pbe2;pbo3;pbo4;n.u.;pbo1;pbo2;ovcorr
 1 1 158.2004 99.1897 78.0000 -0.7738 -0.4550 1.0000 37.6117 0.4147
 0.4590 -0.1000 9.1628 1.0000 -0.0777 6.7268 1.0000 0.0000
 1 2 169.4760 0.0000 0.0000 -0.6083 0.0000 1.0000 6.0000 0.7652
 5.2290 1.0000 0.0000 1.0000 -0.0500 6.9136 0.0000 0.0000

2 2 153.3934 0.0000 0.0000 -0.4600 0.0000 1.0000 6.0000 0.7300
 6.2500 1.0000 0.0000 1.0000 -0.0790 6.0552 0.0000 0.0000
 1 3 158.6946 107.4583 23.3136 -0.4240 -0.1743 1.0000 10.8209 1.0000
 0.5322 -0.3113 7.0000 1.0000 -0.1447 5.2450 0.0000 0.0000
 2 3 160.0000 0.0000 0.0000 -0.5725 0.0000 1.0000 6.0000 0.5626
 1.1150 1.0000 0.0000 0.0000 -0.0920 4.2790 0.0000 0.0000
 3 3 142.2858 145.0000 50.8293 0.2506 -0.1000 1.0000 29.7503 0.6051
 0.3451 -0.1055 9.0000 1.0000 -0.1225 5.5000 1.0000 0.0000
 1 4 124.6651 0.0000 0.0000 0.8374 -0.3000 0.0000 36.0000 0.0100
 1.8311 -0.3500 25.0000 1.0000 -0.2337 4.6603 0.0000 0.0000
 2 4 88.1357 0.0000 0.0000 -0.6715 -0.3000 0.0000 36.0000 0.0208
 9.9192 -0.3500 25.0000 1.0000 -0.1014 5.5268 0.0000 0.0000
 3 4 175.2517 0.0000 0.0000 -0.8707 -0.3000 0.0000 36.0000 0.0100
 0.9278 -0.3500 25.0000 1.0000 -0.1183 4.6533 0.0000 0.0000
 4 4 65.7742 0.0000 0.0000 -0.4111 -0.3000 0.0000 16.0000 0.2955
 2.8637 -0.4197 14.3085 1.0000 -0.1993 4.8757 0.0000 0.0000
 6 ! Nr of off-diagonal terms; Ediss;Ro;gamma;rsigma;rpi;rpi2
 1 2 0.1239 1.4004 9.8467 1.1210 -1.0000 -1.0000
 1 3 0.1156 1.8520 9.8317 1.2854 1.1352 1.0706
 2 3 0.0283 1.2885 10.9190 0.9215 -1.0000 -1.0000
 1 4 0.3393 1.4683 12.5362 1.4713 -1.0000 -1.0000
 2 4 0.0616 1.4846 11.6504 1.6956 -1.0000 -1.0000
 3 4 0.3745 1.8179 9.7359 1.4165 -1.0000 -1.0000

37 ! Nr of angles;at1;at2;at3;Thetao,o;ka;kb;pv1;pv2

1	1	1	59.0573	30.7029	0.7606	0.0000	0.7180	6.2933	1.1244
1	1	2	65.7758	14.5234	6.2481	0.0000	0.5665	0.0000	1.6255
2	1	2	70.2607	25.2202	3.7312	0.0000	0.0050	0.0000	2.7500
1	1	3	49.6811	7.1713	4.3889	0.0000	0.7171	10.2661	1.0463
2	1	3	65.0000	13.8815	5.0583	0.0000	0.4985	0.0000	1.4900
3	1	3	77.7473	40.1718	2.9802	-25.3063	1.6170	-46.1315	2.2503
1	2	1	0.0000	3.4110	7.7350	0.0000	0.0000	0.0000	1.0400
1	2	2	0.0000	0.0000	6.0000	0.0000	0.0000	0.0000	1.0400
1	2	3	0.0000	25.0000	3.0000	0.0000	1.0000	0.0000	1.0400
2	2	2	0.0000	27.9213	5.8635	0.0000	0.0000	0.0000	1.0400
2	2	3	0.0000	8.5744	3.0000	0.0000	0.0000	0.0000	1.0421
3	2	3	0.0000	15.0000	2.8900	0.0000	0.0000	0.0000	2.8774
1	3	1	73.5312	44.7275	0.7354	0.0000	3.0000	0.0000	1.0684
1	3	3	79.4761	36.3701	1.8943	0.0000	0.7351	67.6777	3.0000
1	3	2	70.1880	20.9562	0.3864	0.0000	0.0050	0.0000	1.6924
2	3	2	85.8000	9.8453	2.2720	0.0000	2.8635	0.0000	1.5800
2	3	3	75.6935	50.0000	2.0000	0.0000	1.0000	0.0000	1.1680
3	3	3	80.7324	30.4554	0.9953	0.0000	1.6310	50.0000	1.0783
1	3	4	104.6094	27.2324	9.0549	0.0000	2.3214	0.0000	1.1378
2	3	4	90.0000	11.1212	4.3379	0.0000	3.0000	0.0000	3.0000
3	3	4	43.6280	11.0750	6.6200	0.0000	3.0000	0.0000	1.0100
4	3	4	64.5513	10.5987	1.0471	0.0000	3.0000	0.0000	1.6045

3 4 3 84.7469 7.3926 2.9453 0.0000 0.1000 0.0000 1.2535
 3 4 4 27.4957 14.3276 0.2771 0.0000 2.3158 0.0000 2.2134
 1 4 1 51.9685 44.5007 3.5568 0.0000 1.5137 0.0000 1.0170
 4 1 4 1.0000 32.3336 8.0478 0.0000 0.1476 0.0000 1.0537
 2 1 4 80.6030 30.7117 9.8117 0.0000 0.6965 0.0000 2.1354
 1 4 3 85.0931 44.6258 2.0213 0.0000 1.7462 0.0000 1.1565
 1 1 4 19.4475 2.2656 8.7606 0.0000 2.3143 0.0000 1.6903
 1 4 4 39.3013 12.9114 0.5761 0.0000 3.0000 0.0000 2.8613
 2 4 2 79.7991 0.1000 0.1000 0.0000 1.4104 0.0000 1.4114
 2 4 4 4.0000 25.8806 0.6357 0.0000 0.5039 0.0000 2.3628
 2 4 4 180.0000 -40.0000 2.3424 0.0000 1.2344 0.0000 1.0100
 4 2 4 0.0000 10.9458 0.1218 0.0000 0.1000 0.0000 1.0588
 2 2 4 0.0000 1.4899 1.8813 0.0000 1.5753 0.0000 1.2147
 1 4 2 49.9808 4.4654 7.6824 0.0000 0.1213 0.0000 2.8840
 1 2 4 0.0000 0.1000 0.1300 0.0000 0.6694 0.0000 2.9331
 26 ! Nr of torsions;at1;at2;at3;at4;;V1;V2;V3;V2(BO);vconj;n.u;n
 1 1 1 1 -0.2500 34.7453 0.0288 -6.3507 -1.6000 0.0000 0.0000
 1 1 1 2 -0.2500 29.2131 0.2945 -4.9581 -2.1802 0.0000 0.0000
 2 1 1 2 -0.2500 31.2081 0.4539 -4.8923 -2.2677 0.0000 0.0000
 1 1 1 3 -0.3495 22.2142 -0.2959 -2.5000 -1.9066 0.0000 0.0000
 2 1 1 3 0.0646 24.3195 0.6259 -3.9603 -1.0000 0.0000 0.0000
 3 1 1 3 -0.5456 5.5756 0.8433 -5.1924 -1.0180 0.0000 0.0000
 1 1 3 1 1.7555 27.9267 0.0072 -2.6533 -1.0000 0.0000 0.0000

1 1 3 2 -1.4358 36.7830 -1.0000 -8.1821 -1.0000 0.0000 0.0000
2 1 3 1 -1.3959 34.5053 0.7200 -2.5714 -2.1641 0.0000 0.0000
2 1 3 2 -2.5000 70.0597 1.0000 -3.5539 -2.9929 0.0000 0.0000
1 1 3 3 -2.0000 73.0530 1.5000 -9.0000 -2.0000 0.0000 0.0000
2 1 3 3 0.1933 80.0000 1.0000 -4.0590 -3.0000 0.0000 0.0000
3 1 3 1 -1.9889 76.4820 -0.1796 -3.8301 -3.0000 0.0000 0.0000
3 1 3 2 0.2160 72.7707 -0.7087 -4.2100 -3.0000 0.0000 0.0000
3 1 3 3 -1.8835 20.0000 1.5000 -9.0000 -2.0000 0.0000 0.0000
1 3 3 1 0.0002 80.0000 -1.5000 -2.5000 -2.0000 0.0000 0.0000
1 3 3 2 -2.5000 -3.3822 0.7004 -5.4467 -2.9586 0.0000 0.0000
2 3 3 2 2.5000 -4.0000 0.9000 -2.5000 -1.0000 0.0000 0.0000
1 3 3 3 1.2329 -4.0000 1.0000 -2.5000 -1.7479 0.0000 0.0000
2 3 3 3 0.8302 -4.0000 -0.7763 -2.5000 -1.0000 0.0000 0.0000
3 3 3 3 -2.5000 -4.0000 1.0000 -2.5000 -1.0000 0.0000 0.0000
0 1 2 0 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
0 2 2 0 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
0 2 3 0 0.0000 0.1000 0.0200 -2.5415 0.0000 0.0000 0.0000
0 1 1 0 0.0000 50.0000 0.3000 -4.0000 -2.0000 0.0000 0.0000
0 3 3 0 0.5511 25.4150 1.1330 -5.1903 -1.0000 0.0000 0.0000
1 ! Nr of hydrogen bonds;at1;at2;at3;Rhb;Dehb;vhb1
3 2 3 2.1200 -3.5800 1.4500 19.5000

Appendix B. Typical LAMMPS Input for Minimization

```
# ----- Initialize Simulation -----  
  
clear  
  
units metal  
  
boundary p p p  
  
atom_style atomic  
  
read_data Isobutane.dat  
  
  
# ----- Define Interatomic Potential -----  
  
pair_style meam  
  
pair_coeff * * CH_library.meam C H CH.meam C H  
  
  
# ----- Define Output -----  
  
dump coord all custom 1 Isobutane.dump id type x y z  
  
  
# ----- Run Minimization -----  
  
minimize 1e-25 1e-25 10000 10000
```

Appendix C. Typical LAMMPS Input for NVT Run

LAMMPS input file

```
# REAX potential for CHO system  
  
# .....  
  
unitsreal
```

```

atom_style charge
box tilt large
read_data Al100_with_H2O
pair_style reax/c lmp_control
pair_coeff * *ffield.reax.AlCH2 Al C H O
mass 1 26.9800
mass 2 12.0107
mass 3 1.0080
mass 4 15.999
#velocity all create 300.0 4928459 rot yes dist gaussian
neighbor 2 bin
neigh_modify every 10 delay 0 check no
restart 1000 restart.*.equil
thermo_style custom step temp etotal pe press vol pxx pyy pzz pyz pxz pxy

fix 1 all nvt temp 300.0 300.0 100.0
fix 2 all qeq/reax 1 0.0 10.0 1e-6 reax/c
timestep 0.25
thermo 10
thermo_style custom step temp press etotal
dump 1 all custom 50 dump.output_Al100_18H2O.txt.300k_2 id type q x y z
run 50000

```

Input control

simulation_nameCHO_example ! output files will carry this name + their specific ext

tabulate_long_range10000 ! denotes the granularity of long range tabulation, 0 means no tabulation

energy_update_freq 1

nbrhood_cutoff4.5 ! near neighbors cutoff for bond calculations in Å

hbond_cutoff6.0 ! cutoff distance for hydrogen bond interactions

bond_graph_cutoff0.3 ! bond strength cutoff for bond graphs

thb_cutoff0.001 ! cutoff value for three body interactions

write_freq10000 ! write trajectory after so many steps

traj_titleCHO ! (no white spaces)

atom_info1 ! 0: no atom info, 1: print basic atom info in the trajectory file

atom_forces1 ! 0: basic atom format, 1: print force on each atom in the trajectory file

atom_velocities0 ! 0: basic atom format, 1: print the velocity of each atom in the trajectory file

bond_info1 ! 0: do not print bonds, 1: print bonds in the trajectory file

angle_info1 ! 0: do not print angles, 1: print angles in the trajectory file

Parameter

1 -0.2451 12.6638 .5675

2 5.9666 14 0.9000

3 3.7248 19.2186 .8203

4 8.5000 16.6244 1.0898