First Principles Multiscale Modelling of the Atomic Layer Deposition of Al₂O₃ and ZnO

Timo Weckman
First Principles Multiscale Modelling of the Atomic Layer Deposition of $\text{Al}_2\text{O}_3$ and ZnO

Timo Weckman

A doctoral dissertation completed for the degree of Doctor of Science (Technology) to be defended, with the permission of the Aalto University School of Chemical Engineering, at a public examination held at the lecture hall KE1 of the school on 14th of September 2018 at 12.

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Aalto University publication series
DOCTORAL DISSERTATIONS 161/2018

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ISBN 978-952-60-8149-6 (printed)
ISSN 1799-4934 (printed)
ISSN 1799-4942 (pdf)

Unigrafia Oy
Helsinki 2018

Finland
Abstract

The rapid development of nanotechnology, especially in the field of microelectronics, and ever shrinking dimensions of device components set high requirements for the manufacturing of the necessary nanostructures. Many microscopic components, e.g. transistors, are constructed layer-by-layer from thin film. An important tool 21st century technique for the fabrication of such thin films is the atomic layer deposition. Atomic layer deposition, originally developed in Finland, is based on sequential self-limiting gas-pulses, resulting in a uniform, pin-hole free thin film, with thickness control at the atomic level.

Computational modeling is an important part of modern chemistry. Research can be conducted theoretically - without empirical parameters - with the application of quantum mechanics. With quantum mechanical calculations it is possible to model the electronic structure of molecules and to study the bonding and interactions of molecules as well as different molecular mechanisms. In this work, the deposition of aluminium and zinc oxides were studied using computational chemistry. Both oxides have wide range of applications e.g. in transistors and solar cells.

Aluminium oxide is usually deposited using a trimethylaluminium-water-process. The surface chemistry was studied on a realistic hydroxylated surface model and trimethylaluminium was observed to react rapidly with surface hydroxyl groups to produce monomethylaluminium. Monomethylaluminium was estimated to be relatively inert and to convert to aluminium only at high temperatures. Subsequent water pulse mechanisms were also studied at low methyl-coverage. Direct dimethylaluminium-water reactions were accessible at process conditions, but the elimination of monomethylaluminium by water requires a complex cooperative mechanism.

Zinc oxide is usually deposited using a diethylzinc-water-process. Diethylzinc was found to convert rapidly into monoethylzinc but the elimination of monoethylzinc was found to be a slow process. Based on the calculations, two ethyl-saturated surface structures were constructed, corresponding to low and high temperature estimations. These saturated surfaces were used in a subsequent study on the water pulse reactions, resulting in a reaction network for a complete ALD cycle.

The growth of the zinc oxide thin film was then modeled in macroscopic scale using a kinetic Monte Carlo model. The kinetic modelling enables a direct comparison with experimental measurements. The kinetic model, built upon the theoretical calculations, accurately predicted the temperature-dependency of the film growth. Also, the predicted growth per cycle is in good agreement with experimental data.

Keywords atomic layer deposition, density functional theory, kinetic Monte Carlo


Avainsanat: atomikerrokskasvatust, tiheysfunktioaaliteoria, kineettinen Monte Carlo
Preface

This thesis has been prepared in the Computational Quantum Chemistry group in the Department of Chemistry and Materials Science at Aalto University School of Chemical Engineering. The work was funded by the Academy of Finland and the computational resources used were graciously provided by the CSC, the Finnish center for scientific computing.

I wish to thank Professor Kari Laasonen for the opportunity to pursue a doctorate in computational chemistry and for providing an interesting topic in a rather fresh research field. I am grateful for the support he has given me, of the encouraging discussions we have had and for the freedom he has granted me in pursuing my research. I am also very grateful to my collaborators Dr. Mahdi Shirazi and Dr. Simon Elliott for their help, expertise and example.

I also wish to thank the people, past and present, of the Aalto physical chemistry community, especially my co-candidates. The atmosphere in our lab has always been warm and inspiring and people rarely say no to beer, especially my co-candidates.

Last, but not least, I wish to thank my family and friends for their support and interest in my work. I am especially happy for the support and love I have received from my wife and for the balance our family-life has brought to my life.

Espoo, August 22, 2018,

Timo Weckman
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List of Publications

This thesis consists of an overview and of the following publications which are referred to in the text by their Roman numerals.

I Timo Weckman, Kari Laasonen. First principles study of the atomic layer deposition of alumina by TMA-H$_2$O-process. *Physical Chemistry Chemical Physics*, 17(26), 17322-17334 2015.


Author’s Contribution

Publication I: “First principles study of the atomic layer deposition of alumina by TMA-H$_2$O-process”

The author did the literature survey, conducted the DFT calculations and the analysed data. The research plan was defined and the paper was written in collaboration with prof. Kari Laasonen, who also supervised the research work.

Publication II: “Atomic Layer Deposition of Zinc Oxide: Diethyl Zinc Reactions and Surface Saturation from First-Principles”

The author did the literature survey, conducted the DFT calculations and the analysed data. The research plan was defined and the paper was written in collaboration with prof. Kari Laasonen, who also supervised the research work.

Publication III: “Atomic Layer Deposition of Zinc Oxide: Study on the Water Pulse Reactions from First Principles”

The author did the literature survey, conducted the DFT calculations and the analysed data. The research plan was defined and the paper was written in collaboration with prof. Kari Laasonen, who also supervised the research work. Dr. Simon D. Elliott assisted in interpreting the data.
Author’s Contribution

Publication IV: “Kinetic Monte Carlo Study of the Atomic Layer Deposition of Zinc Oxide”

The author implemented the DFT calculations into the kinetic Monte Carlo code in collaboration Dr. Mahdi Shirazi and Dr. Simon D. Elliott. The kinetic Monte Carlo application was originally developed by Dr. Mahdi Shirazi and Dr. Simon D. Elliott. The data was analyzed in collaboration with all the authors. Major part of the paper was written by the author, in collaboration with Dr. Mahdi Shirazi and Dr. Simon D. Elliott and prof. Kari Laasonen
### List of abbreviations and symbols

#### Abbreviations

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<td>Atomic Layer Deposition</td>
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<td>Diethylzinc</td>
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<td>DFT</td>
<td>Density Functional Theory</td>
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<td>HK</td>
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<td>Perdew–Burke–Ernzerhof functional</td>
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<td>TMA</td>
<td>Trimethylaluminium</td>
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List of abbreviations and symbols

**Symbols**

\( T \)  
Temperature

\( p \)  
Pressure

\( E \)  
Energy

\( k_B \)  
Boltzmann constant

\( h \)  
Planck constant

\( m_e \)  
Mass of an electron

\( M_A \)  
Mass of an atomic nucleus \( A \)

\( \varepsilon_0 \)  
Permittivity of free space

\( e \)  
Elementary charge

\( h \)  
Reduced Planck constant

\( \beta \)  
\( 1/k_B T \)

\( \hat{H} \)  
Hamiltonian operator

\( \Psi \)  
Wave function

\( Z_A \)  
Charge of an atomic nucleus \( A \)

\( \mathbf{R}_A \)  
Position of an atomic nucleus \( A \)

\( \mathbf{r}_i \)  
Position of an electron \( i \)

\( \mathbf{x}_i \)  
Position and spin of an electron \( i \)

\( \hat{T} \)  
Kinetic energy operator for electrons

\( V_{\text{ext}} \)  
Potential energy operator acting on electrons due to nuclei

\( v_{\text{ext}}(\mathbf{r}) \)  
Potential energy for electron \( \mathbf{r} \)

\( \hat{W} \)  
Potential energy operator for inter-electronic interactions

\( w(\mathbf{r}_i, \mathbf{r}_j) \)  
Potential energy between particles \( \mathbf{r}_i \) and \( \mathbf{r}_j \)

\( n(\mathbf{r}) \)  
Electron density

\( T_s \)  
Kinetic energy of independent-particle system

\( F[\rho] \)  
The Hohenberg–Kohn functional

\( \mu \)  
Chemical potential

\( \omega \)  
Electrophilicity

\( \eta \)  
Chemical hardness
1. Introduction

The rapid progress in the field of nanotechnology in the recent decades, especially in microelectronics, has lead to the shrinking of nanodevice components. To meet this demand, evermore higher standards are required from the manufacturing processes. Many microscopic instruments, like transistors, are constructed layer-by-layer from thin films. Atomic layer deposition (ALD) is a process used for growing uniform, high quality thin films with thickness control at the atomic level. In the past two decades, it has emerged as an important coating technique with various industrial applications in nanotechnology in the present day.

Atomic layer deposition has been invented independently two times, first in the Soviet Union in the 1960s and subsequently in Finland in the 1970s. The ALD as it is known today is the offspring of the pioneering work done by Dr. Suntola and his group, an achievement for which Dr. Suntola was awarded the Millennium prize in 2018. ALD is based on alternating, self-limiting surface reactions of the gaseous precursors that are separated by inert gas purges. This leads to cyclic growth with growth per cycle of the order of an atomic layer.

The fundamental understanding of the growth of the thin film lies on the mechanistic interpretation of the surface reactions; the conceptual view of the process is based on what surface reactions contribute to the deposition of the film. Much of what happens on the surface is beyond the experimental tools commonly used to study the deposition process. Therefore, theoretical simulations based on quantum mechanics can help to identify the key steps in the process and bring insight on the overall deposition process.

Theoretical investigation of atomic layer deposition has been a rising
Introduction

field in past few decades. Computational chemistry can be used to obtain both qualitative and quantitative insight to the surface reactions contributing to the growth of the thin film. Modelling of the deposition process can be done on multiple time- and length-scales depending on the choice of the model.

In this work, the atomic layer deposition of Al$_2$O$_3$ and ZnO thin films were investigated using quantum chemistry and kinetic modelling. For both processes, the key surface reaction mechanisms are investigated using density functional theory (DFT). It can be assumed that an ALD process is mainly controlled by surface kinetics, since most of the surface processes are irreversible. DFT can be used to investigate the adsorption of the precursor molecules and the subsequent ligand elimination reactions on the surface. From the energetics of these reactions, the kinetics for the surface processes can be obtained and the evolution of the process understood.

In addition to the atomic scale calculations, the mechanisms obtained from the DFT calculations were used to construct a reaction network for the overall deposition process. Using the calculated energetics for each mechanism, a time-dependent model for the growth of the thin film can be constructed and with a kinetic Monte Carlo (kMC) algorithm, the dynamical growth can be predicted without empirical parameters. Data obtained from the kinetic model can be more readily compared with the usual experimental data and this serves as an important quantitative and qualitative validation of the DFT calculations.
2. Atomic Layer Deposition

Atomic layer deposition (ALD) is an important thin film deposition technique with various applications in modern technology. ALD allows for the deposition of high quality thin films with extreme thickness control. In ALD, the reactants, precursors, are introduced into the reactor chamber separately, thus avoiding any gas-phase reactions. The reactants are chosen so that the adsorption and surface reactions for each precursor is self-limiting. All the chemical reactions are restricted to take place on the surface as the reactor chamber is purged with inert gas between alternating reactant pulses. A sequence of reactant pulses results in a growth of a thin film. The deposited films are uniform, pin-hole free and the process allows the film thickness to be controlled at the atomic level by repeating the growth cycle desired number of times.1

2.1 History and future outlooks

The atomic layer deposition has been invented independently twice by two groups in neighbouring countries. The ALD principle of alternate self-limiting surface reactions was first documented by professor Aleskovskii and his group in Soviet Union in the 1960s. Inorganic materials were deposited using molecular precursors and the process was dubbed "molecular layering (молекулярное наслаивание)". A similar process was developed in Finland in the 1970s by Dr. Tuomo Suntola and his co-workers2 dubbed "atomic layer epitaxy" (ALE). The Soviet-Russian origins were not known even to Suntola himself until the 1990s. The Finnish origin of ALD has since become widely known as the development of ALE lead to applications in thin film electroluminescent flat panel displays in the 1980s.3–5
Figure 2.1. Number of articles on the topics of "atomic layer deposition" and "density functional theory" published per year (orange) as well as articles published per year on "atomic layer deposition" or "atomic layer epitaxy" (black).
Source: Web of Science, accessed on January 30, 2018

Dr. Suntola was awarded the Millennium Technology Prize for the development of ALD in 2018.6

Over time the process was titled atomic layer depositions, since the growth of the thin film was not necessarily epitaxial. The first ALD-conference was held in Finland in the 1984 and the first international conference, also in Finland, in 1990.

Interest in ALD has increased exponentially over the years as shown in figure 2.1. The number of scientific articles published remained steady through the 1990s but started to grow rapidly after the change of the millennium. Similarly, the theoretical modelling of ALD has seen an increase over the years. However, the roots of theoretical modelling of ALD extend back to the beginning of ALD itself. Theoretical quantum chemical investigations of zinc sulphide were already presented in the first symposium on atomic layer epitaxy in 1984 by Tapani Pakkanen7.

ALD has become a prominent method in thin film deposition and has
great prospects for the future. The set of possible materials that can be deposited is large and expanding\textsuperscript{8} and different special techniques based on the ALD procedure, such as atomic layer etching\textsuperscript{9} and area selective ALD\textsuperscript{10}, are gaining interest.

2.2 ALD process

The principle of ALD is simple: by separating the gaseous reactants to two separate pulses, the overall chemistry of the system is simplified as all the relevant chemistry occurs on the substrates surface. The reactants, dubbed precursors, are molecules containing a given element A (such as a metal, oxygen, sulphur etc.) coordinated to some reactive ligand X. For example, aluminium oxide is deposited using trimethylaluminium (TMA, here $A = \text{Al}$, $X = \text{CH}_3$) and water ($A = \text{O}$, $X = \text{H}$). The precursors are chosen so that they react violently with one another but do not react with themselves. By introducing the precursors into the reactor in separate pulses, the chemical reactions between the reactants are restricted to occur only on the surface. The reactants undergo a ligand-exchange reaction on the surface, producing a composite of the given elements and releasing a (preferably) inert by-product from the reacted ligands. In the case of TMA/H$_2$O, the process produces aluminium oxide, Al$_2$O$_3$, and releases methane, CH$_4$, as a by-product.

A general ALD cycle of the TMA/H$_2$O process is summarized in figure 2.2. A small dose of the metal precursor (TMA) is introduced into the reactor within a carrier gas, such as nitrogen. The precursor then adsorbs to the surface and undergoes a ligand-exchange reaction, losing one or more of its ligands. The precursors are chosen so as to have no gas-phase reactions with each other and, hence, the adsorption process terminates when the surface is fully covered. The reactor is then purged with an inert gas to remove any excess precursor molecules or reaction by-products. After purging, the second precursor (water, H$_2$O) is introduced. Water adsorbs to the surface and undergoes a ligand-exchange reaction with the remaining TMA fragments. After saturation, the reactor is again purged. The thin film has grown a monolayer in thickness and the surface is ready for another cycle.
Atomic Layer Deposition

Figure 2.2. An illustration of an ideal ALD cycle during Al₂O₃ deposition with trimethylaluminium/water. First, the hydroxylated aluminium oxide surface is saturated with TMA, resulting in dimethylaluminium and monomethylaluminium fragments. The subsequent water pulse ideally removes the surface methyl-ligands and substitutes them with hydroxyl groups, restoring the surface for another cycle.

The thin film growth rates (nm/s) in ALD are relatively low if compared to other thin film deposition methods, such as chemical vapor deposition (CVD). A typical ALD cycle takes few seconds for completion, resulting ideally in one monolayer of growth. This monolayer-per-cycle growth rate is rarely observed in practice as the steric hindrance of the reactants usually forbids a full monolayer coverage. However, the slow growth rate is not considered a major obstacle as the thin film thickness required in modern technology applications usually range from just a few nanometers to few dozen nanometers and the slow deposition rate is balanced out by the thickness control.¹

Due to the alternation of the precursor pulses and the self-limiting nature of the surface reactions, ALD growth is independent of the substrate geometry. This leads to a uniform growth of the thin film and ALD can be utilized to very large substrate surface areas. The uniform growth is nicely illustrated in figure 2.3 where Al₂O₃ thin films have been grown on a patterned silicon substrated using ALD. The Al₂O₃ films have equal thickness within the trenches of the silicon substrate as on top of the...
The high quality of ALD thin films is, at least ideally, due to the strict control of the environmental variables. Because the chemical reactions during deposition are restricted to the surface and due to the low pressure of the precursors, the main variable is the deposition temperature. In literature, the optimal deposition temperature range where the ALD process fulfils the requirement of self-terminating reactions is referred to as the "ALD window". In this range, the growth-per-cycle (GPC) is usually nearly constant and the thin film thickness can be controlled by changing the number of deposition cycles. A usual GPC vs. temperature profile is illustrated in figure 2.4 for the DEZ/H2O process.

In this work we focus on computational modelling of thermal homodeposition of aluminium and zinc oxides using ALD. The precursors used in this work are trimethylaluminium and water (TMA/H2O) for Al2O3 and diethylzinc and water (DEZ/H2O) for ZnO. These are also the most common precursors used to deposit these thin films. The relevant chemical processes contributing to the growth of the thin film are obtained using density functional theory. For the zinc oxide process, chemical reaction rates are computed based on the theoretical calculations and a kinetic model for the overall thin film growth is constructed.

### 2.3 ALD surface reactions

The main molecular processes in ALD are the flow of the gaseous precursors into the reactor, the chemical interaction between the gaseous pre-
Atomic Layer Deposition

Figure 2.4. A quartz crystal microbalance measurement of the ALD of zinc oxide. The growth-per-cycle shows clear temperature dependency. The so-called "ALD window" is the plateau from approximately 130 °C to 180 °C. Reprinted with permission from ref 12.

cursors and the substrate surface and the atomic level rearrangement on the surface. In this work we will focus only on the gas-solid interactions and the general dynamics of the precursors flow as well as any surface relaxations are neglected. The central chemical processes related to the growth of the thin film are adsorption and desorption of the precursors and surface reaction pathways of the adsorbed species.

Adsorption means the bonding of a gaseous molecule onto a solid interface. Depending on the strength of the chemical bond, adsorption can be divided into physisorption and chemisorption. Physisorption originates from weak, secondary chemical bonds caused by van der Waals interactions. Physisorption is not specific for the molecule–surface pair and can occur in several layers. In chemisorption, a new chemical bond is formed between the surface and the molecule, possibly leading to a simultaneous breaking of other bond(s). Because the chemisorption is molecule–surface specific, only a monolayer of molecules can adsorb; hence, virtually all the adsorption relevant to thin film growth in ALD is chemisorption.

The fundamental aspect of ALD is that the adsorption of each precursor pulse is self-terminating. Therefore, it is essential that precursor molecules do not react with each other in gas-phase or on the surface. This limits the range of possible precursors as well as usually requires rather modest deposition temperatures relative to other deposition methods to avoid pyrolysis of the precursor molecules.

The adsorption is self-terminating either because of the saturation of
Figure 2.5. Adsorption process for trimethylaluminium (TMA) where the adsorption is terminated due to a) the saturation of all the available adsorption sites and b) the inhibition caused by steric effects. It is usually not clear which of the two cases takes place during the deposition.

all the suitable adsorption sites or inhibition due to steric effects between precursor ligands. The saturation of all the reactive sites is illustrated in figure 2.5a. When all the reactive sites have been saturated, no new chemisorption bonds can be formed between the precursors and the surface and only a weakly bound physisorped second layer can be formed. If all the reactive sites are not exhausted, then the saturation is due to steric hindrance between the adsorbed precursors as illustrated in figure 2.5b. The ligands shield possible reactive sites and make them inaccessible to other incoming molecules. Fully saturated surface does not necessarily lead to a monolayer deposition rate of the thin film; a monolayer of metal oxide is not necessarily deposited per each ALD cycle. This is because the adsorbed surface species take more than their share of space on the surface. Whether the surface saturation is due to exhaustion of the reactive sites or due to steric hindrance between the adsorbants, varies from system to system and may be temperature dependent.

For the adsorption process to be irreversible, the precursor must form a strong chemical bond with the substrate. This usually occurs via a ligand-exchange reaction, whereby one of the precursors ligands combine with a ligand of a surface group to produce a volatile (and preferably inert) by-product. In the case of a generic metal precursor $ML_z$ with $z$ ligands, the ligand-exchange reaction can be written as a two-step process: the precu-
Atomic Layer Deposition

sor first forms an adsorption bond and then reacts with a surface group:\(^3\)

\[
\| - \text{OH} + \text{ML}_z \rightarrow \| - \text{OH-ML}_z
\]

\[
\| - \text{OH-ML}_z \rightarrow \| - \text{O-ML}_{z-1} + \text{HL}
\]

Other reaction pathways are also possible. If no reactive surface sites are present to exchange ligands with, the adsorbed precursor can dissociate on the surface by donating a ligand to a surface site:\(^3\)

\[
\| - \text{M} + \| - \text{O} \xrightarrow{\text{ML}_z} \| - \text{ML} + \| - \text{O-ML}_{z-1}
\]

Due to the inert nature (and the low partial pressure) of the by-product, the ligand-exchange reaction can usually be considered irreversible and the remaining surface group can no longer desorb from the surface. The fragments can react further with other surface groups to eliminate more ligands, but this does not lead to bonding of more metal-atoms onto the surface. The average number of removed ligands \(x\) can vary with temperature.\(^3\)

2.4 In situ Experimental Methods

The focus of this work is to use quantum mechanics to describe the relevant surface chemistry contributing to the growth of the thin film. There exists a scale-difference of several orders of magnitude between an ab initio calculation consisting of few dozen up to a hundred atoms and an experimental ALD study, that usually focuses on the macroscopic descriptors of a thin film, such as average GPC and physical properties of the film. Mapping the atomic-scale calculations to the macroscopic quantities is not straightforward, so a brief review of experimental methods that provide crucial, direct or indirect, experimental data on the surface mechanisms – and possible validation of the calculations – is presented here.

The most relevant continuous in situ methods used for studying ALD reaction mechanisms are mass spectrometry (MS), quartz crystal microbalance (QCM) and infrared spectrometry (IR).\(^5\)

**Fourier transform infrared spectroscopy (FTIR)** is a non-destructive method that enables in situ information on the nature of the chemical bonds broken and formed on the surface during deposition\(^{13}\). FTIR can also be used to identify what by-products are formed during deposition.
FTIR has been used to study the deposition of both aluminium and zinc oxide thin films which are the subject of this study.\textsuperscript{14–18}

**Quadrupole mass spectrometry (QMS)** can be used to measure the gaseous species present in the reactor during the deposition process and especially to identify the by-products of the growth reactions.\textsuperscript{5,13} The molecules in the outflow of the reactor are ionized and fragmented by electrons from a filament source and then sorted by their mass/charge-ratio \(m/z\) in the quadrupole analyser. The main limitation of this procedure is in attributing the \(m/z\)-ratio signal to a single fragment, as the same ratio can be obtained through different processes.

In QMS measurements on ALD, it is a common practise to first pulse the reactor chamber with one precursor several times, then to pulse the precursors alternatively (resulting in deposition of the film) and then to pulse several times the second precursor only. For ALD processes where the surface reaction is a pure ligand-exchange reaction mechanism, interpreting the QMS data is straightforward.\textsuperscript{5}

**Quartz crystal microbalance (QCM)** allows measuring microscopic changes in mass during the deposition of a thin film. The QCM is based on the piezoelectric resonance of the quartz crystal that changes as a response to a change in mass which can then be measured. This allows us to observe in high precision the time-evolution of the deposition.

### 2.5 ALD of Al\(_2\)O\(_3\)

Aluminium oxide thin films have wide range of applications and they can be grown with various precursor combinations. In this work, the ALD of Al\(_2\)O\(_3\) was studied using trimethylaluminium and water as precursors. This process is one of the most studied ALD-process and is considered to be a model ALD system.\textsuperscript{5,8} The first experimental publications on the ALD of Al\(_2\)O\(_3\) using TMA and water were published all the way back in the late 1980s and early 1990s.\textsuperscript{19,20}

The growth of Al\(_2\)O\(_3\) by TMA/H\(_2\)O can be described with the two half-reactions

\begin{align*}
\text{A-1) } & \quad x \underset{-}{\text{OH}} + \text{Al(CH}_3\text{)}_3 \rightarrow \underset{-}{\text{O}_2 \cdot \text{Al(CH}_3\text{)}_3 - x} + x \text{CH}_4 \\
\text{A-2) } & \quad \underset{-}{\text{O}_2 \cdot \text{Al(CH}_3\text{)}_3 - x} + (3 - x) \text{H}_2\text{O} \rightarrow \underset{-}{\text{O}_2 \cdot \text{Al(OH)}_3 - x} + (3 - x) \text{CH}_4
\end{align*}
where $x$ is the average number of hydroxyl groups that react with an adsorbed TMA. Stoichiometric film is grown with $x = 1.5$, but experimentally $x$ is estimated to be around 1.5 to 1.7$^{21}$. The overall surface chemistry of A-1 and A-2 has been confirmed by FTIR experiments$^{14-17}$. The adsorption of both precursors is self-limiting and the change from a hydroxyl covered surface into a methyl-saturated surface and back can be observed from the infrared spectra. The linear growth trend can also be observed from the integrated absorbance of the bulk oxide. 

$\text{Al}_2\text{O}_3$ thin films can be deposited at temperatures as low as 33 °C$^{22}$ and TMA/H$_2$O-process yields well-defined films up to 177 °C. The low deposition temperature enables deposition even unto thermally fragile substrates such as polymers. The as-deposited $\text{Al}_2\text{O}_3$ thin films have an amorphous structure.$^{23}$

The growth-per-cycle of alumina is about 1.1 Å.$^{15,16}$ The GPC is much lower than would be expected for a process with an ideal monolayer growth rate for which the GPC would be 3.8 Å. The amount of aluminium deposited onto the surface has been shown to insensitive to the reaction temperature. However, the surface hydroxyl concentration is temperature-dependent and a heat treatment of the substrate before deposition decreases in the surface hydroxyl concentration. The decrease in the number of surface hydroxyl groups is observed to decrease the amount of aluminium deposited onto the surface, leading to a decrease of the overall growth rate. The amount of aluminium adsorbed $\Delta c_{\text{Al}}$ depends linearly on the surface hydroxyl concentration $c_{(\text{O})\text{H}}$,$^{24}$

$$\Delta c_{\text{Al}} = 1.68 + +0.37c_{(\text{O})\text{H}}$$  \hspace{1cm} (2.1)$$
where the concentrations $c_{\text{Al}}$ and $c_{(\text{O})\text{H}}$ are given in units of nm$^{-2}$. The equation has a direct physical interpretation. The intercept equals one third of the number of methyl groups adsorbed during the TMA adsorption on a dehydroxylated $\text{Al}_2\text{O}_3$ surface with no OH-groups. This is reasonable, as each TMA produces three methyl-ligands onto the surface. The slope gives the average amount of aluminium atoms deposited per added OH-group. Thus, roughly three hydroxyl groups are needed to add an additional aluminium atom onto the surface. The surface methyl concentration has been observed to be virtually independent of the surface
hydroxyl-group concentration.\textsuperscript{24}

While the general chemistry of the TMA/H\textsubscript{2}O-process is well understood, the research on the surface kinetics and mechanisms are still lacking as the surface kinetics of ALD are difficult to measure experimentally. Some estimates of the overall kinetics have been extracted. For example, Dillon \textit{et al.}\textsuperscript{14} conclude that the water half-reaction is roughly 3.8 times faster than the TMA half-reaction at 1.3 Pa pressure and 500 K temperature. Dillon \textit{et al.}\textsuperscript{14} note that the absorbance data does not suggest initial formation of surface $-$CH\textsubscript{3}-species as initially the decrease in surface AlO$-$H absorbance is not met with an increase in C$-$H\textsubscript{3} stretching absorbance.

An interesting recent study by Vandalon and Kessels\textsuperscript{25} shows that the ideal picture of the deposition process is incomplete. The authors investigated the cause for the decrease in GPC at low temperatures. When an O\textsubscript{2} plasma is used as the oxygen source in the process, the thin film growth profile remains relatively stable at temperatures as low as 100°C, while for thermal ALD with H\textsubscript{2}O there is an observable decrease in the GPC. To study the cause of this decrease in the GPC, Vandalon and Kessels used a broadband sum-frequency generation (BB-SFG) technique to investigate the surface chemistry of Al\textsubscript{2}O\textsubscript{3} during deposition. The signals measured using BB-SFG can be directly correlated to absolute surface density, unlike commonly used differential techniques such as FTIR. This way they were able not only to measure surface species that were changing during deposition, but also species that persisted after an ALD cycle.

The authors find that at temperatures 200°C and below, a fraction of the CH\textsubscript{3}-ligands persist on the surface after the water pulse, even though saturation is reached. The authors propose\textsuperscript{26} that this is either caused by ligand-coverage dependent surface kinetics or due to some unreactive surface ligands and find some support for the former hypothesis. The conclusion by Dillon \textit{et al.}\textsuperscript{14} of the relative rates between TMA and H\textsubscript{2}O does not seem to hold at lower temperatures. The incomplete elimination of the methyl-ligands is a surprising result as it is usually assumed (and concluded in experiments) that all the surface ligands are removed during the deposition.
2.6 ALD of ZnO

Zinc oxide is a wide band-gap semiconductor with broad set of properties that can be utilized in applications e.g. high transparency, tunable electrical conductivity and piezoelectric properties.27–29 The most common precursors for zinc oxide ALD are diethylzinc (DEZ) and water. Much like the TMA/H2O-process, the ALD of ZnO via DEZ/H2O is close to an ideal ALD process, as the precursors react violently with one another, are not chemically active in the gas-phase and the reaction by-products are highly volatile and inert.

The DEZ/H2O-process can be separated into the following half-reactions:12,18,30

Z-1) \[ \parallel - \mathrm{OH} + \text{Zn}(\mathrm{CH}_2\mathrm{CH}_3)_2 \rightarrow \parallel - \mathrm{O} - \text{Zn}(\mathrm{CH}_2\mathrm{CH}_3) + \mathrm{CH}_3\mathrm{CH}_3 \]

Z-2) \[ \parallel - \mathrm{O} - \text{Zn}(\mathrm{CH}_2\mathrm{CH}_3) + \mathrm{H}_2\mathrm{O} \rightarrow \parallel - \mathrm{O} - \text{ZnOH} + \mathrm{CH}_3\mathrm{CH}_3. \]

Thus, the main reactions are assumed to be the adsorption of a DEZ with the loss of one of its ligand (Z-1) and a subsequent reaction between the monoethylzinc (MEZ) and water during the water pulse (Z-2).

The temperatures usually used in deposition of zinc oxide range from 100 to 200 °C. The as-deposited thin films are polycrystalline with various lattice orientations present and these orientations are sensitive to temperature. At low and high deposition temperatures (below 100 °C and above 200 °C) the (002) orientation is dominant. However, the (002) orientation diminishes between temperatures 100 °C and 200 °C and the (100) orientation becomes slowly dominant, reaching its peak at 160-200 °C.31–33

The growth-per-cycle (GPC) of a zinc oxide ALD-process ranges from 1.7 to 2.1 Å depending on the deposition temperature.12 This corresponds to about 60% to 80% from an ideal monolayer growth.

A lot of research has been done in the recent years to understand the specific surface reactions taking place during deposition. After the surface has been saturated with DEZ, it is assumed that all the surface ethyl-ligands are removed during the subsequent water pulse resulting in a hydroxylated surface at the end of the ALD cycle.12,34 Assuming that the main product from the DEZ pulse is monoethylzinc, there would an observable negative mass-change in the film, since in the overall reaction the heavy ethyl-ligands would be replaced by much lighter hydroxyl groups. However, the mass-change measured using quartz-crystal mass-
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balance (QCM)\textsuperscript{12} is slightly positive for the water pulse. One proposed explanation for this is the presence of bare zinc atoms on the surface in addition to the monoethylzinc groups. These bare zinc sites could adsorb more water onto the surface and balance out the mass-change from the ligand-exchange reaction. Ferguson \textit{et al.}\textsuperscript{18} have suggested the pyrolysis of diethylzinc as a possible mechanism to produce bare surface zinc atoms.

Just as in the case of Al\textsubscript{2}O\textsubscript{3}, it has been recently observed that some of the carbonyl-ligands persist on the surface after the water pulse. Mackus \textit{et al.}\textsuperscript{35} conducted an \textit{in situ} gas-phase and surface FTIR spectroscopy measurements on the ALD of zinc tin oxide (ZTO) thin films and noticed that after a typical water exposure, 30-50\% of the surface ethyl-ligands persisted on the surface during the growth of a ZnO thin film. Even after extended periods of water exposure, approximately 16\% of surface ethyl-ligands remain on the surface at 150 °C temperature and only at elevated temperatures around 200 °C virtually all the ligands were removed from the surface. The authors conclude that there is a high kinetic barrier for removing some of the ligands from surface during the water pulse.

### 2.7 Computational Studies of ALD

Computational modelling of atomic layer deposition has been growing in the past few years. There have been two reviews\textsuperscript{36,37} of the field in general. A short review of the computational literature relevant to the thesis is presented here. The focus is on the previous computational studies related to the ALD of aluminium and zinc oxides as well as on kinetic Monte Carlo simulation of ALD.

The ALD of Al\textsubscript{2}O\textsubscript{3} via TMA/H\textsubscript{2}O-process was first studied by Widjaja and Musgrave\textsuperscript{38}. The simulation was based on a cluster-model, whereby the surface environment is represented by a small atomic cluster instead of modelling the surface with a periodic slab. The TMA was found to form an Lewis acid–base adduct onto a surface hydroxyl group and a barrier for the ligand-exchange was calculated to be of the order of 0.5 eV. The subsequent water pulse reactions with the surface dimethyl- and monomethylaluminium had higher barriers of 0.7 eV and 0.9 eV, respectively. Shankar \textit{et al.}\textsuperscript{39} also conducted a similar cluster-model study.
Elliott and Greer\textsuperscript{40} studied the same process using a periodic model, where the surface was represented by a finite slab with periodic boundary conditions. While as-deposited aluminium oxide thin films are in reality amorphous, the authors used crystalline alumina in their calculations. The most stable facet of (0001) \( \alpha \)-alumina was chosen as the substrate. The surface was terminated with a gibbsite, Al(OH)\(_3\), layer to include hydroxylation.\textsuperscript{41} The calculations for the formation of the Lewis adduct by Elliott and Greer\textsuperscript{40} agree with those obtained from the cluster model\textsuperscript{38}. However, they find that the proton transfer occurs most readily with a neighboring hydroxyl group. The authors also observe that TMA adsorption is very exothermic even on bare Al\(_2\)O\(_3\) surface, so ALD growth can be expected to occur even in the complete absence of hydroxyl groups, which is confirmed by experiments\textsuperscript{3,24}. The reaction energies were found to be very exothermic, in agreement with the cluster model, and the resulting by-product methane was found to desorb readily from the surface.

The study by Elliott and Greer\textsuperscript{40} focused on the initial stages of the deposition when the surface coverage is low. The influence of neighboring surface fragments (dimethylaluminium, monomethylaluminium) at higher coverage was studied by Shirazi and Elliott.\textsuperscript{42} They found that the activation energy for proton transfer and ligand elimination was substantially reduced by the presence of neighbouring surface fragments. They termed the phenomena of neighbouring adsorbates influencing the kinetics on the surface as a 'cooperative effect'. The acidity/basicity of the surface seems to be strongly depend on the coverage of the fragments.

Studies on the ALD of zinc oxide are far fewer than on aluminium oxide, although the ALD process has similar advantages from a modelling point of view: the DEZ/H\(_2\)O process is self-saturating, it has a well-defined ALD windows and the by-product ethane is nonpolar, inert molecule. The atomic layer deposition of zinc oxide via DEZ/H\(_2\)O-process has been studied on hydroxylated silicon by Ren\textsuperscript{43} and on hydroxylated zinc oxide by Afshar and Cadien\textsuperscript{44} using a cluster-model. Afshar and Cadien\textsuperscript{44} report that DEZ forms a moderately strong adsorption bond with the cluster, but that the reaction barriers for ethyl elimination are high. Tanskanen \textit{et al.}\textsuperscript{45} studied the reaction free energies for binding of tetrakis(dimethylamido)tin (TDMASn) and DEZ on various OH-terminated zinc oxide surfaces using a periodic slab-model. They compared thermodynamic stability of differ-
ent surface species and concluded that the consumption of reactive hydroxyl sites by multi-ligand TDMASn leads to the reduced growth of zinc oxide after a TDMASn pulse. In their study, the authors did not investigate the kinetics of these processes or the saturation limit of the surface during the deposition.

Studies employing kinetic Monte Carlo simulations to study ALD growth from first principles exist for HfO\(_2\), ZrO\(_2\) and Al\(_2\)O\(_3\). Deminsky et al.\(^{46}\) studied the deposition of HfO\(_2\) and ZrO\(_2\) films based on \emph{ab initio} cluster model calculations. Their model was able to produce the correct temperature dependence of the growth rate of the film and also to describe the accumulation of chloride atoms in the growing thin film. Mazaleyrat et al.\(^{47}\) constructed a kMC model for the heterodeposition of Al\(_2\)O\(_3\) on Si. Neizvestny et al.\(^{48}\) studied the relationship between surface nucleation and growth rate. HfO\(_2\) was also studied by Dkhissi et al.\(^{49,50}\) with activation energies extracted from cluster model calculations. The authors investigated the effect of surface hydroxylation on the initial growth of the thin film.

A kinetic Monte Carlo model built on a periodic slab model calculations was done by Shirazi and Elliott\(^{51}\). The authors studied the Hf(N(CH\(_3\))\(_2\))\(_4\)/H\(_2\)O-process for HfO\(_2\) ALD using reaction rates based on DFT calculations on explicit surface\(^{52}\). The model accounted for the steric hindrance between the ligands and included cooperative effects of the neighbouring adsorbates on the reaction barriers. The growth rates obtained from the model were within 20\% of experimental data.

Other kinetic models based on theoretical calculations have also been used to study atomic layer deposition. Travis and Adomaitis\(^{53}\) used the reaction barriers obtained by Elliott and Greer\(^{40}\), Widjaja and Musgrave\(^{38}\) and Delabie et al.\(^{54}\) in a kinetic model of the TMA/H\(_2\)O-process. The authors conclude that the surface hydroxylation is a key factor in the growth rate of the film.

This work expands on the previous research by studying the TMA/H\(_2\)O process on a more realistic Al\(_2\)O\(_3\) surface model (publication I). The reaction mechanisms for the DEZ/H\(_2\)O process are investigated in detail using a periodic surface model (publications II-III). This mechanistic data is then implemented into a kinetic Monte Carlo model developed by Shirazi and Elliott and used to predict the thin film growth of zinc oxide from first
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principles (publication IV).
3. Theoretical Methods

The surface chemistry relevant to atomic layer deposition can be modelled with quantum mechanics. Theoretical foundation for the structure of matter was laid out in the 1920s by Heisenberg, Schrödinger, Bohr, Einstein and others. The many-body quantum mechanics derived in the 1930s, mainly the Hartree–Fock theory and its derivatives, such as configuration interaction (CI) and Møller–Plesset perturbation theory (MPPT), provide the theoretical framework used in physics and chemistry and are powerful tools for producing accurate predictions in molecular chemistry.

Deviating from the traditional quantum mechanics is the density functional theory (DFT). While the Hartree–Fock method, and the derivatives thereof, are extremely powerful tools in molecular quantum chemistry, the computational complexity of these models makes them unusable for large periodic systems. DFT is an answer to this problem. Instead of attempting to solve $3N$-dimensional electronic wave function of the quantum mechanical system, DFT reframes the problem and solves the electronic structure with respect to the electron density. This requires some crucial approximations but dramatically decreases the computational cost and provides reasonable results in turn.

Within the past half a century, the computational methods for studying matter at atomic scale have improved significantly and computational chemistry can be applied to large systems consisting of hundreds of atoms. The structure of chemical compounds, physical properties, reactivity and thermochemistry can be studied both quantitatively and qualitatively. However, it is difficult to deduce the evolution of the thin film growth from the surface reaction energetics alone. Therefore, kinetic modelling is required to bridge the gap between atomic scale calculations and macro-
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Figure 3.1. A rough illustration of various simulation models at different length and time scales. Quantum mechanics (QM) and transition state theory (TST) are situated in the angstrom length and picosecond time scales. With molecular dynamics (MD), a nanosecond time scale can be reached. Kinetic Monte Carlo (kMC) allows extending the ab initio reaction rates into a larger time scales of milliseconds or beyond. With a kinetic model, also the length scale can be extended several orders of magnitude. At reactor scale modelling continuum models can be used to include for e.g. flow dynamics within the reactor, but the atomic scale description is usually treated in an approximate manner.

scopic experimental measurements (see figure 3.1). In this work, kinetic Monte Carlo (kMC) is used to model the overall growth process of the zinc oxide thin film, based on density functional theory calculations.

In this section, the approaches used in the thesis will be presented. Density functional theory, as implemented in GPAW, was used to model the atomic scale chemical reactions. The minimum energy pathways (MEP) defining the transitions from a given state to the next were computed using the nudged elastic band (NEB) method. Reaction rates were calculated with transition state theory (TST). These rates were then employed into the kinetic model where the nonlinear differential equations were solved using kinetic Monte Carlo (kMC) as implemented in the SPPARKS package.

3.1 Molecular Electronic Structure Theory

The fundamental equation in quantum mechanics is the Schrödinger equation. The aim in quantum chemistry is to find (or more accurately, approximate) a solution to the time-independent, non-relativistic Schrödinger
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equation,

\[ \hat{H}\Psi_n(x_1, \ldots, x_N; R_1, \ldots, R_M) = E_n\Psi_n(x_1, \ldots, x_N; R_1, \ldots, R_M) \]  (3.1)

where \( \hat{H} \) is the Hamiltonian or total energy operator and \( \Psi_n \) is the wave function of the \( n \)th state of the system. The equation is fundamentally an eigenvalue equation for the operator \( \hat{H} \) where \( E_n \) is the eigenvalue corresponding to the \( n \)th eigenstate. \( \hat{H} \) is a differential operator and for a system of \( N \) interacting spin-1/2 particles and \( M \) nuclei, it can be written out as

\[ \hat{H} = \hat{T} + \hat{V}_{\text{ext}} + \hat{W} \]  (3.2)

where \( \hat{T} \) is the kinetic operator,

\[ \hat{T} = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 \]  (3.3)

and \( \hat{V}_{\text{ext}} \) is the interaction of the electrons with external time-independent potential,

\[ \hat{V}_{\text{ext}} = \sum_{i=1}^{N} v_{\text{ext}}(r_i) \]  (3.4)

and \( \hat{W} \) is the particle–particle interaction,

\[ \hat{W} = \frac{1}{2} \sum_{i,j=1,i\neq j}^{N} w(r_i, r_j). \]  (3.5)

For a molecular system the inter-particle interactions between the electrons and nuclei are Coulombic interactions. The external potential in a molecular system is a static field produced by the nuclei

\[ \hat{V}_{\text{ext}} = \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{|R_A - r_i|}. \]  (3.6)

The electron–electron interaction in eqn 3.5 is described by a Coulombic interaction,

\[ w(r_i, r_j) = \frac{e^2}{4\pi\epsilon_0 \left| r_i - r_j \right|}. \]  (3.7)

The wave function \( \Psi_n \) can be thought of as the probability amplitude of the system, describing deterministically the time evolution of the system. The wave function contains all the information that can possibly be known of the quantum system. The lowest energy eigenstate, \( \Psi_0 \), is called the ground state of the system.
For brevity, one can write the Schrödinger equation in atomic units and dispense with the constants. Then the Hamiltonian takes the form

\[ \hat{H} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}_i|} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \]  

(3.8)

For many-body systems consisting of several electrons, the direct integration of the Schrödinger equation becomes practically impossible and approximations must be carried out in order to make the computation feasible. For this reason, the most common approximations (Born–Oppenheimer) and approaches (Hartree–Fock and Density functional theories) taken in solving the Schrödinger equation are introduced.

### 3.1.1 Born–Oppenheimer approximation

A chemical system consists of atomic nuclei and electrons. Due to difference in the relative mass between the electrons and nuclei (nuclei–electron mass-ratio is 1800 or larger depending on the nuclei), the movement of the electrons and nuclei can be decoupled. The total wave function of the system is therefore usually separated into the electronic and the nuclear wave functions, so the total wave function can be written as a product:\(^{55}\)

\[ \Psi_{\text{total}}(\mathbf{r}, \mathbf{R}; t) = \Psi_{\text{elec}}(\mathbf{r}; \mathbf{R})\Psi_{\text{nuc}}(\mathbf{R}; t). \]  

(3.9)

This is called the Born–Oppenheimer approximation proposed in 1927\(^{56}\) and it is essential in molecular quantum mechanics. Due to the large mass of the nuclei, the inner structure of the nuclei and its quantum nature are usually omitted and the nuclei are treated as classical particles characterized only by their charge and mass.

In Born–Oppenheimer scheme, the electronic wave function is solved for fixed configuration of the nuclei. The total energy consists of the nuclear potential, electronic kinetic energy, electron–electron repulsion and electron–nuclear attraction. The electron inertia is assumed negligible. In a molecular system, the nuclei are subject to forces caused by the electrons and these forces can be obtained from the electronic wave function by the Hellmann–Feynman theorem. Since the nuclei are treated as classical particles, the total force (electronic force + nuclear repulsion) can be used to find a minimum energy structure or to study molecular dynamics using the Newtonian equations of motion.\(^{55}\)
3.1.2 Hartree–Fock theory

A standard approach for solving a differential equation is to use a separable trial function. In many-body quantum theory this means an ansatz written as a product of one-electron wave functions, orbitals. However, for a fermionic quantum system one must require that the trial function remains antisymmetric with respect to permutations among the electrons. An antisymmetric wave function of a product form can be generated by a *Slater determinant*, where each column \( i \) and row \( j \) consists of an spin-orbital \( \phi_i \) with an electron \( j \):

\[
|\Psi\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\phi_1(r_1\sigma_1) & \cdots & \phi_N(r_1\sigma_1) \\
\vdots & \ddots & \vdots \\
\phi_1(r_N\sigma_N) & \cdots & \phi_N(r_N\sigma_N)
\end{vmatrix}
\]

(3.10)

where \( \sigma_i \) denotes the spin of the particle \( i \). A spin-orbital \( \phi_i \) is a product of a spatial orbital and a spin function.

The foundation for all approximate theories in quantum mechanics are built upon the variational principle. The variational principle states, that the exact ground state energy is the lower bound for the expectation value of the total energy that can be calculated. Thus, any trial wave function that approximates the exact ground state wave function will result in an expectation value above the exact ground state energy and the approximation can be enhanced by minimizing the expectation value of the total energy with respect to the trial wave function.

In Hartree–Fock method\(^{57,58}\), an antisymmetric product wave function is used to minimize the expectation value of total energy with respect to the one-electron wave functions. This minimization scheme, subject to spin-orbital orthonormality, produces a set of nonlinear integro–differential-equations for each orbital, called the Hartree–Fock equations,

\[
\hat{f} \phi_i = \epsilon_i \phi_i \\
\hat{f} = \hat{T} + v_{\text{ext}}(r) + v_{\text{HF}}(r\sigma, r'\sigma')
\]

(3.11)

where \( \hat{f} \) is the Fock-operator and \( \epsilon_i \) is an eigenvalue corresponding to the orbital \( \phi_i \). The Fock-operator is a sum of the kinetic energy of an electron \( \hat{T} \), the electron–nuclear attraction between the nuclei and the electron \( v_{\text{ext}}(r) \) and a mean-field interaction term \( v_{\text{HF}} \). The mean-field interaction
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term consists of the direct Coulombic interaction (Hartree potential) $v_H$ and the exchange potential $v_{\text{HF}}^x$,

$$v_{\text{HF}}(\mathbf{r}\sigma, \mathbf{r}'\sigma') = v_H(\mathbf{r}) + v_{\text{HF}}^x(\mathbf{r}\sigma, \mathbf{r}'\sigma'). \quad (3.12)$$

The Hartree potential $v_H$ is defined as

$$v_H(\mathbf{r}) = \int d\mathbf{r}' w(\mathbf{r}, \mathbf{r}') \sum_{\sigma'} \sum_{j=1}^N \left| \phi_j(\mathbf{r}' \sigma') \right|^2. \quad (3.13)$$

The Coulomb repulsion represents the average repulsion between electron $i$ and another electron at orbital $\phi_j$. The exchange potential can written out explicitly as

$$v_{\text{HF}}^x(\mathbf{r}\sigma, \mathbf{r}'\sigma') = -\sum_{\sigma'} \int d\mathbf{r}' w(\mathbf{r}, \mathbf{r}') \sum_{j=1}^N \phi_j(\mathbf{r}\sigma) \phi_j^*(\mathbf{r}'\sigma'). \quad (3.14)$$

The exchange term $v_{\text{HF}}^x$ arises from the antisymmetric form of the wave function and is a uniquely quantum mechanical interaction.

The Hartree–Fock equations are essentially pseudo-Schrödinger equations for each electron that average the inter-electron repulsion in a mean-field way. The equations are also nonlinear, since solving the equations for orbital $i$ depends on having a solution for every other orbital in the system. Thus, the solution needs to be determined in an iterative manner. This is called the self-consistent field (SCF) method. In SCF, an initial guess of the orbitals is first obtained in some way, for example using an extended Hückel method\textsuperscript{59} or some variant thereof. The Hartree–Fock equations are then solved resulting in a new set of orbitals. These orbitals are in turn used for solving the Hartree–Fock equations. The loop is continued until a pre-set threshold for convergence is achieved.

Hartree–Fock theory was developed in the 1930s and is a powerful first-order approximation for the molecular electronic structure and provides reasonable estimates for molecular bond lengths and angles. The method has, however, severe shortcomings in other aspects. The Hartree–Fock method allows for a direct way of obtaining the exact solution (exact within the given basis set) called configuration interaction. This approach is, however, not practical due to the computational demand of the method. Several other improvements, dubbed post-Hartree–Fock methods, have since been devised, such as Møller–Plesset perturbation theory and coupled cluster method, that are computationally demanding, but can be utilized for rather large systems of molecules.
An entirely different approach called the density functional theory allows for solving the total energy of the system without trying to obtain the wave function. The problem is reformulated in terms of the square of the wave function, the electron density. By writing the total energy as a functional of electron density, the dimensionality is reduced from $3N$-dimensional wave function to just 3-dimensional electron density. In theory, as in practice, this makes for a computationally cheaper alternative for obtaining a solution to the Schrödinger equation.

### 3.1.3 Density Functional Theory

The density functional theory has become the standard tool for studying many-body quantum mechanics in large systems. The rigorous theoretical foundation for the density-based approach was laid in 1964 by Hohenberg and Kohn with the introduction of the Hohenberg–Kohn theorems. Here we will present the basic theory of density functional theory and discuss the approximations commonly used.

#### Hohenberg–Kohn theorems

The fundamental theorems in density functional theory are the Hohenberg–Kohn (HK) theorems. The first HK theorem states that there exists a one-to-one correspondence between the ground state electron density $n_0$ and the external potential $v_{\text{ext}}$. The proof of this theorem is a simple *reductio ad absurdum*. The statement of the theorem given here applies to a non-degenerate ground state of electrons in an electrostatic external potential. The statement needs to be slightly modified for degenerate states or if a static magnetic field is included.

Due to the one-to-one correspondence, the ground state $|\Psi_0\rangle$ is a unique functional of the ground state density $n_0$, $|\Psi_0\rangle = |\Psi[n_0]\rangle$. The existence of this functional means that any ground state observable $O$ is a functional of the density:

$$O[n] := \left\langle \Psi[n] \right| \hat{O} \left| \Psi[n] \right\rangle$$  \hspace{1cm} (3.15)

In particular, this is true for the ground state energy. The total energy of
The system gives the most important density functional:

\[
E[n] := \langle \Psi[n] | H | \Psi[n] \rangle = F[n] + \int dr v_{\text{ext}}(r) n(r)
\]

\[
F[n] = \langle \Psi[n] | \hat{T} + \hat{W} | \Psi[n] \rangle
\]  

(3.16)

where \( F[n] \) is called the Hohenberg–Kohn functional, a universal part of the total energy functional that is independent of a given system. The external potential \( v_{\text{ext}} \), on the other hand, is system specific and is defined by the positioning of the atomic nuclei or other external sources.

The second HK theorem states that there exists a minimum principle for \( E[n] \): if \( n_0 \) is the ground state electron density corresponding to \( v_{\text{ext}} \), then for all densities \( n'_0 \neq n_0 \):

\[
E[n_0] < E[n'_0]
\]  

(3.17)

and so the ground state electron density can be searched by minimizing the total energy functional with respect to the density

\[
E_0 = \min_{n \rightarrow n_0} \left( F[n] + \int dr v_{\text{ext}}(r) n(r) \right).
\]  

(3.18)

The HK theorems suggest that the total energy and all other subsequent properties of a many-particle system can be recovered from the ground state electron density alone. However, the theorems provide no guide toward actually obtaining the ground state electron density and energy. For this reason, different methods for actually calculating the ground state density and energy have been developed, the Kohn–Sham method being perhaps the most successful.

**Kohn–Sham method**

Let us consider a system with the Hamiltonian (eqn 3.2) with a non-degenerate ground state. In the Kohn–Sham\textsuperscript{62} framework, two systems with equal ground state densities are created: a real, fully interacting system and a fictitious non-interacting system. The non-interacting system serves as a mathematical tool for calculating most of the kinetic energy via Hartree–Fock-type orbitals, since there exists no known method of accurately obtaining the kinetic energy from electron density. The non-interacting system consists of \( N \) electrons that have no electron–electron interaction (other than the Pauli exclusion principle) but that experience
an external potential $\hat{V}_s$ that produces the same ground state density as
the fully interacting system.

The Hamiltonian for the non-interacting system is

$$\hat{H}_s = \hat{T} + \hat{V}_s, \quad \hat{V}_s = \int \text{d}\mathbf{r}\hat{n}(\mathbf{r})v_s(\mathbf{r})$$

(3.19)

where the external potential $v_s$ is multiplicative potential used to bridge
the non-interacting and the fully interacting systems. The ground state
solution for a non-interacting fermionic particles is a Slater determinant
$|\Phi_0\rangle$ (eqn 3.10) and the minimum energy solution for the non-interacting
system is obtained from the usual one-particle eigenvalue problem of

$$\left(\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right)\phi_i(\mathbf{r}\sigma) = \epsilon_i\phi_i(\mathbf{r}\sigma).$$

(3.20)

The eigenvalues $\epsilon_i$ are assumed to be ordered as

$$\epsilon_1 \leq \epsilon_2 \leq \ldots \leq \epsilon_N = \epsilon_F \leq \epsilon_{N+1} \leq \ldots$$

(3.21)

where $\epsilon_F$ is the Fermi-energy, equal to the eigenvalue of the highest occu-
pied orbital $\epsilon_N$. The ground state density $n_{0s}$ for system in eqn 3.19 can
be obtained from the orbitals,

$$n_{0s} = \sum_{\sigma} \sum_{i=1}^N |\phi_i(\mathbf{r}\sigma)|^2 = 2 \sum_{\alpha=1}^{N/2} |\phi_\alpha(\mathbf{r})|^2.$$  

(3.22)

The HK theorems apply to systems with an arbitrary inter-particle in-
teraction $w(\mathbf{r}, \mathbf{r}')$. For the non-interacting system the interaction term
is zero, and thus the non-degenerate ground state density in eqn 3.22 is
unique and the ground state of a non-interacting system is a unique func-
tional of the ground state density, $|\Phi[n]\rangle$, with $|\Phi_0\rangle = |\Phi[n_0]\rangle$. The ground
state energy of the non-interacting system is

$$E_s[n] = \langle \Phi[n] | \hat{T} + \hat{V}_s | \Phi[n] \rangle = \sum_{i=1}^{N} \epsilon_i$$

$$+ \int \text{d}\mathbf{r}\hat{n}(\mathbf{r})v_s(\mathbf{r}).$$

(3.23)

The total energy of the fully interacting system is also a functional of the
density:

$$E[n] = T_s[n] + E_H[n] + E_{\text{ext}}[n] + E_{\text{xc}}[n]$$

(3.24)

where $T_s$ is the kinetic energy of the electrons. This can be obtained from
the non-interacting system since $|\Phi[n]\rangle$ is universal. $E_H$ is the classical
Hartree interaction between $N$ particles with density $n$:

$$E_H[n] = \frac{1}{2} \int \int \text{d}\mathbf{r}\text{d}\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

(3.25)
and $E_{\text{ext}}$ is the interaction between the electron density and the external potential created by the $M$ nuclei:

$$E_{\text{ext}} = \sum_{A=1}^{M} \int d\mathbf{r} \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_A|}. \quad (3.26)$$

The final term in eqn 3.24 is the *the exchange and correlation energy*, $E_{\text{xc}}[n]$. The exchange and correlation energy absorbs all the complicated many-body interactions that are not contained in $T_s, E_H$ or $E_{\text{ext}}$, such as the exchange energy due to the antisymmetric form of the wave function, electron–electron correlation and the difference in the kinetic energy between interacting and non-interacting electrons.

The non-interacting and fully interacting systems are linked through the external potential $v_s$,

$$v_s(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{H}[n_0](\mathbf{r}) + v_{\text{xc}}[n_0](\mathbf{r}) \quad (3.27)$$

where

$$v_{H}[n_0](\mathbf{r}) = \int d\mathbf{r}' w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') \quad (3.28)$$

and

$$v_{\text{xc}}[n_0](\mathbf{r}) = \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}. \quad (3.29)$$

Inserting this into eqn 3.20, we get the *Kohn–Sham equations*,

$$\left(-\frac{1}{2} \nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_{H}[n_0](\mathbf{r}) + v_{\text{xc}}[n_0](\mathbf{r})\right) \phi_i(\mathbf{r} \sigma) = \epsilon_i \phi_i(\mathbf{r} \sigma) \quad (3.30)$$

These equations need to be solved self-consistently in a similar fashion to the Hartree–Fock equations.

The functionals $T_s, E_H, E_{\text{ext}}$ and $E_{\text{xc}}$ are universal. This means that the same xc-functional applies to all systems where the particle–particle interaction is given by the Coulomb force. Approximations made to obtain $E_{\text{xc}}$ can therefore be utilized to any system.

The form of the $E_{\text{xc}}$ remains unknown and various density functional approximation have been devised to model the exchange–correlation effects. The exchange–correlation part of the total energy is usually relatively small and complete neglect of the $E_{\text{xc}}$ leads to qualitatively correct electron structure. However, from the point of view of chemistry this portion is extremely important, since in chemistry we are usually interested in energy differences between configurations. Next, commonly used approximate functionals are presented.
3.1.4 Local density approximation (LDA)

A first approximation for the exchange–correlation energy is the local density approximation. In LDA, the exchange and correlation energies are obtained from a model system for which the density-dependence is known. The LDA is appropriate only if the electron density does not change rapidly within the system, since the exchange–correlation contribution is based on a system of uniform electron distribution.

The many-body problem of \( N \) interacting electrons can be solved explicitly only for some special cases, most notably for the homogeneous electron gas (HEG), an infinite system of uniform electron gas with a given electron density \( n = \frac{N}{V} \). The HEG is balanced out by a uniform positive charge so that, in total, the system is neutral. Since the system is infinite in size, only the energy density \( e = \frac{E}{V} \) of the system is meaningful. For HEG, the exchange energy can be solved exactly and the electron correlation at various densities can be solved numerically.

In LDA, the exchange–correlation energy density \( \epsilon_{xc} \) becomes a function of the density \( n(\mathbf{r}) \) instead of a functional. The exchange–correlation energy can be written as

\[
E_{\text{LDA}}[n] = \int n(\mathbf{r}) \epsilon_{xc}(n(\mathbf{r})) d\mathbf{r}
\]  

(3.31)

where the energy density \( \epsilon_{xc} \) is split into exchange and correlation contributions,

\[
\epsilon_{xc}(n(\mathbf{r})) = \epsilon_x(n(\mathbf{r})) + \epsilon_c(n(\mathbf{r})).
\]  

(3.32)

The exchange part of the energy can be calculated exactly for the HEG. This was done by Bloch and Dirac in the late 1920s,

\[
\epsilon_x(n(\mathbf{r})) = -\frac{3}{4} \sqrt{\frac{3n(\mathbf{r})}{\pi}}.
\]  

(3.33)

No such explicit expression is known for \( \epsilon_c \). The correlation part is usually adopted from highly accurate quantum Monte Carlo simulations for the HEG. LDA has been used successfully for decades in computational solid state physics, since the electron density in a solid metallic system does not vary rapidly. However, LDA performs poorly for molecular systems and is not applicable in chemistry.
3.1.5 Generalized gradient approximation (GGA)

LDA can be improved by including the local inhomogeneity at \( r \) by adding a gradient to the energy density,

\[
\epsilon_{x/c}^{\text{GGA}} = \epsilon_{x/c}^{\text{LDA}} + \Delta \epsilon_{x/c} s(r)
\]  (3.34)

where \( s(r) = \frac{|\nabla n(r)|}{n_{\sigma}(r)} \) is the so-called reduced density gradient. This kind of functional is called the generalized gradient approximation (GGA). A wide variety of such functionals exist, some constructed ab initio with no parameters, other parametrized to high accuracy calculations and some fitted to reproduce experimental data.

The exchange part of the exchange–correlation energy can be written as

\[
E_x^{\text{GGA}} = E_x^{\text{LDA}} - \sum_\sigma \int F(s_\sigma(r)) n^{4/3}_\sigma(r) \, dr
\]  (3.35)

where the summation is over the two different spins \( \sigma \). \( F \) depends on the approximate functional used. For the Perdew–Burke–Ernzerhof (PBE) functional used in this work, we have

\[
F_x(s) = 1 + \kappa - \frac{\kappa}{1 + \mu^2/\kappa}
\]  (3.36)

where \( \mu = 0.21951 \) and \( \kappa = 0.804 \).

The reduced density gradient \( s \) describes the local inhomogeneity of the electron density. \( s \) is large when the gradient is large but also when the density is small e.g. far from the nucleus. Equally, \( s \) is small when the density is nearly constant or when the density is large e.g. in an interatomic bond. The gradient correction significantly improves the bond energies calculated using DFT but in some cases overcorrects the LDA.

The PBE functional is a good overall functional that contains no fitted or empirical parameters and it is often employed for solid state physics and surface chemistry simulations. PBE improves on LDA on all aspects and provides a good description of molecular systems, adsorption energies, reaction barriers and bond lengths and angles. PBE has been the basis for several derivative functionals such as revPBE, RPBE and PBEsol.

3.1.6 Other approaches

Several other approaches have been taken to further improve the approximations in exchange–correlation functionals. A logical extension of the
GGA approach is to add a second derivative i.e. the Laplacian of the electron density or the kinetic energy density into the functional. This increases the flexibility of the functional and the resulting functionals are dubbed meta-GGA functionals. A meta-GGA functional usually somewhat outperforms a GGA functional.\textsuperscript{67} Perhaps the most commonly employed meta-GGA functional is the TPSS functional.\textsuperscript{71}

Another commonly used subset of functionals are the so-called hybrid functionals. In hybrid functionals, the approximate density functional is improved by replacing a fraction of local or semi-local exchange functional with the exact exchange functional obtained from the Kohn–Sham orbitals. This partially corrects for the problematic self-interaction error present in approximate functionals. The hybrid functionals greatly improve the overall performance of the approximate functional.\textsuperscript{67,72} However, the calculation of the exact exchange comes with a computational cost. Perhaps the most commonly used hybrid functionals are the B3LYP\textsuperscript{73} and PBE0\textsuperscript{74} functionals, but there is vast range of hybrid functionals proposed in the literature.\textsuperscript{75}

### 3.1.7 Dispersion interactions

Van der Waals interactions in general are a set of weak interactions between molecules and/or atoms. However, van der Waals interaction is also often used interchangeably with London dispersion interaction that results from quantum fluctuations in the electron density.\textsuperscript{76} This weak dispersion interaction is an important phenomenon in weakly interacting systems such as between non-polar molecules and atoms and is therefore of importance in chemistry.

Due to the approximate way in which in the electron–electron correlation is treated in DFT, the weak dispersion interaction is not included in any of the standard approximate density functionals. Therefore, the interaction is usually added post-hoc as an attractive, exponentially decaying potential of the form $-C_6/R^6$, where the coefficients $C_6$ are either calculated before hand or from the electron density.\textsuperscript{77–81} Van der Waals corrections are nowadays essential as they significantly improve the description of the functional with minimal costs.\textsuperscript{72}

In this work, the PBE functional is used together with the TS09 van der
Waals correction proposed by Tkatchenko and Scheffler. The TS09 is a nonempirical approach where the dispersion coefficients are derived from the electron density of a molecule and an accurate reference data for the free atoms. The Tkatchenko–Scheffler van der Waals correction greatly improves PBEs ability to describe weak interactions.

3.1.8 Projector augmented wave-method

In this work, the main implementation of density functional theory used is the grid-based projector augmented-wave (GPAW) method for solving the electronic structure of finite or infinitely large systems.

The projector augmented-wave (PAW) method is a computational tool used in GPAW to remove the core-electrons from the calculations to decrease computational cost and improve convergence. The inner most electrons do not partake in chemical bonds and are therefore inert. However, the core electrons of an atom usually have high kinetic energy. Therefore, the corresponding wave functions have a rapidly oscillating form which is difficult to reproduce. Also, the electron–nucleus potential diverges as \( r \to 0 \). In order to get rid of the core electrons, the actual wave function is truncated into a pseudo wave function and the potential produced by the electrons is replaced with an effective core potential.

Projector augmented-wave method is a linear transformation between the smooth valence pseudo (PS) wavefunctions, \( \tilde{\psi}_n \), and the all-electron (AE) wavefunctions \( \psi_n \). The core states \( \phi_i^{a, \text{core}} \) of an atom \( a \) are fixed to the reference shape of an isolated atom. Given a smooth pseudo-wavefunction, the corresponding all-electron wavefunction is obtained through the linear transformation

\[
\psi_n(\vec{r}) = \hat{T} \tilde{\psi}_n(\vec{r}). \tag{3.37}
\]

The transformation operator \( \hat{T} \) is given in terms of atom-centred AE partial waves, \( \phi_i^a \), the corresponding smooth partial waves, \( \tilde{\phi}_i^a \), and projector functions, \( \tilde{p}_i^a(\vec{r}) \), as

\[
\hat{T} = 1 + \sum_a \sum_i \left( |\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle \right) \langle \tilde{p}_i^a |. \tag{3.38}
\]

The AE partial waves and smooth PS partial waves are equal outside the atom-centred augmentation spheres of radii \( r_c \), that is

\[
\phi_i^a(\vec{r}) = \tilde{\phi}_i^a(\vec{r}) \quad \text{when} \quad |\vec{r} - \vec{R}_i^a| > r_c \tag{3.39}
\]
where $\vec{R}^a$ is the position of an atom $a$. The projector functions are localized inside the augmentation spheres and are orthogonal to the PS partial waves, $\langle \tilde{p}^a_{i1} | \tilde{\phi}^a_{i2} \rangle = \delta_{i1,i2}$. An all-electron calculation for a spherically symmetric atom is used to construct the projectors and partial waves. For an exact transformation, the number of atom-centered partial waves and projectors is infinite, but in practice few functions per angular momentum channel is sufficient.\(^8^4\)

In GPAW, the Kohn–Sham and Poisson equations are discretized with a uniform real-space grids. Wavefunctions, densities, potentials and other physical quantities are represented by the values at the grid points. The accuracy of the discretization depends on the finite difference approximations and the grid spacing used but good accuracy is usually obtained with grid spacing of $h = 0.2$ Å.\(^8^4\) Grid calculations are easy to parallelize and, hence, suitable for modern super-computers.

### 3.2 Surface chemistry

The actual surface chemistry of atomic layer deposition is modelled by constructing an atomic level model for the substrate surface and calculating precursor adsorption energies as well as surface reaction barriers at various stages of the deposition. This data can then be used in interpreting the progression of the overall process.

#### 3.2.1 Computational surface model

There are essentially two approaches to study surface chemistry \textit{ab initio}: a cluster model and a surface slab model. In a cluster model, the surface is described with a small atomic cluster consisting of few dozen atoms. In the surface slab model the surface consists of an infinitely large, two-dimensional slab of finite thickness. The infinite size of the slab is due to periodic boundary conditions in the plane of the slab. The slab model is the more realistic one of the two approaches. The cluster model allows for fast and computationally cheap simulations, so more systems can be explored in a given time, but the validity of the model used is difficult to determine and the results usually differ from those done on a slab model for a similar system. In this work, the surface is modelled using the peri-
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The structure of a surface depends on the lattice orientation used to cleave the surface from the bulk. The orientation is defined using Miller indices, \((h k l)\) where \(h, k\), and \(l\) define a normal vector \(h \mathbf{b}_1 + k \mathbf{b}_2 + l \mathbf{b}_3\) for the plane which is cleaved. The vectors \(\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3\) are the basis of the reciprocal lattice vectors.

When a surface is cleaved from the bulk, there is a disruption in the inter-atomic forces. This disruption is highly dependent on the lattice orientation and is quantified as the surface energy. In this work, the surface energy is used as a convergence criterion for the suitable thickness of the slab used in the DFT calculations. The thickness of the surface slab is sufficient when the surface energy of the slab has converged.

The surface energy, \(E_{\text{surface}}\), can be expressed as a limit

\[
E_{\text{surface}} = \lim_{n \to \infty} \frac{E_n - kE_{\text{bulk}}}{2A}
\]  

(3.40)

where \(E_{\text{bulk}}\) is the energy of a stoichiometric unit calculated from the bulk, \(E_n\) is the energy of the surface slab with \(n\) layers, \(k\) is the number of stoichiometric units in the surface slab \(E_n\) and \(A\) is the surface area of the slab.

However, if the \(E_{\text{bulk}}\) is calculated from a periodic bulk system, as is often suggested in the literature, it turns out that the surface energy diverges. This divergence is illustrated in figure 3.2. A convergent value is obtained when the bulk energy is calculated as the slope of the slab energies plotted as a function of the slab size. This approach was used in generating both the \(\text{Al}_2\text{O}_3\) and \(\text{ZnO}\) surface slabs. From the figure 3.2, it is evident that the surface energy for \(\text{ZnO}\) surface has converged after six oxygen layers, which is the slab thickness used in the simulations for zinc oxide.

### 3.2.2 Transition State Theory

Within the Born–Oppenheimer approximation, the configurations of the nuclei span a potential energy surface (PES). Minima on this surface correspond to stable structures and the energy differences between the minima can be used to evaluate the relative thermodynamic stability of the configurations. Around each minima is a hypersurface, the transition state, and passing this surface leads to the basin of another minimum con-
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Figure 3.2. On the left, the computed surface energies as a function of slab thickness are depicted for the two different methods discussed in the text. When the bulk value of a stoichiometric unit in the equation 3.40 is calculated directly from a bulk value, the computed surface energy diverges (red curve). However, if one calculates the bulk value of the stoichiometric unit from the slope of the slab energy with respect to the slab thickness, as proposed by Fiorentini and Methfessel, one obtains a convergent surface energy (blue curve). On the right, the total energy of the slab as a function of the slab thickness is presented. The slope value was obtained from the linear fit to the data points from 6 to 16 ZnO layers.

The chemical reaction can be seen as a transition on the potential energy surface of the system from the potential energy minimum of the initial state to the minimum of the final state. Transition state theory (TST) describes transitions between different minima and can be used to evaluate rates at which the transitions occur at finite temperature. The transition state energy can be obtained from a saddle point in between the two minima of the initial and final states as discussed in 3.2.4.

The canonical transition state theory is based on the assumption that the initial and final states as well as the transition state follow the Boltzmann distribution. The particles crossing the transition state are treated as classical particles and quantum effects (i.e. tunneling) are neglected. The particles are also assumed to cross the transition state only once. The rate constant for a chemical reaction can then be expressed as the flux crossing the transition state,

$$k(T) = \frac{k_B T}{h} \frac{Q^\dagger}{Q} e^{-\Delta E^\dagger/k_B T}$$

(3.41)

where $T$ is temperature, $Q$ and $Q^\dagger$ are the partition functions of the initial and transition states, respectively. $\Delta E^\dagger$ is the energy difference between
the initial and transition states, often called the activation energy.\textsuperscript{87}

3.2.3 Adsorption

Adsorption rate onto a surface can be derived from the kinetic gas theory.\textsuperscript{88} The adsorption rate to the surface is expressed as the particle flux times the area of the adsorption site,

\[ r_{\text{ads}} = \frac{P\sigma(\theta, T)}{\sqrt{2\pi mk_B T}} A \]  

(3.42)

where \( P \) is the pressure of the gaseous reactant, \( \sigma \) is the sticking coefficient of the adsorbant, which is usually set to unity at low surface coverage, \( T \) is temperature of the system, \( m \) is the mass of the particle and \( A \) is the area of the adsorption site.

If the adsorption rate is calculated from the particle flux, it is implicitly assumed that the particle retains translational degrees of freedom on the surface, as well as all the rotational and vibrational modes. This leads to an overestimation of the adsorption rate, since at least some translational and rotational modes are lost when a strong adsorption bond is formed. The adsorption rate calculated from the particle flux, although commonly used, is best suited to describe physisorption. If one assumes that the movement of the particle is restricted to the adsorption site, then the appropriate rate for adsorption would be

\[ r_{\text{ads}} = \frac{P\sigma(\theta, T)\hbar^2}{(2\pi mk_B T)^{3/2}} \]  

(3.43)

where \( \hbar \) is the Planck constant.\textsuperscript{87} In eqn 3.43, the adsorbed molecule retains the rotational and vibrational degrees of freedom after adsorption. There exists two to three orders of magnitude difference in these two expressions. However, the former expression is commonly used and is supported by experimental data as many adsorbed molecules retain a large portion of their entropy after adsorption, a somewhat surprising result.

The desorption can be thought of as a chemical reaction where the molecule is removed from the surface into the gas-phase. The activation energy for the desorption reaction is then equal to the adsorption energy (if the adsorption is barrierless). The rate coefficient for desorption is then given by

\[ k_{\text{des}} = \frac{k_B T}{\hbar} \exp \left( \frac{E_{\text{ads}}}{k_B T} \right). \]  

(3.44)
3.2.4 Nudged Elastic Band method (NEB)

There are several suggested methods for actually finding a suitable transition state for a given reaction.\textsuperscript{90–92} For large systems, finding a transition state becomes evermore expensive. One approach is to probe the possible pathway from a given initial state to the final state by dividing the path between the two configurations into "images", usually generated by interpolating the $xyz$-coordinates. These replicas are then connected to each other by an artificial harmonic force and all the images are optimized simultaneously. The harmonic force prevents the replicas from sliding down the potential energy surface either to the minimum of the initial state or the final state, which ever is closest. The replicas then span the pathway between the initial state and the final state and provide a minimum energy path between the two states. The minimum energy path is characterized by a saddle point that separates the two energy minima.

One such method is called the nudged elastic band (NEB) method.\textsuperscript{90} In NEB, a reaction path vector $\hat{\tau}_i$ is defined for each image $i$,

\begin{equation}
\hat{\tau}_i = \begin{cases} 
\tau_i^+ = R_{i+1} - R_i, & \text{if } E(R_{i+1}) > E(R_i) > E(R_{i-1}) \\
\tau_i^- = R_i - R_{i-1}, & \text{if } E(R_{i+1}) < E(R_i) < E(R_{i-1}) 
\end{cases}
\end{equation}

In the case where the potential energy of image $i$ is an extremum, then the path is taken as a weighted average of $\tau_i^+$ and $\tau_i^-$. The vector $\hat{\tau}_i$ is normalized.

Second, the forces used to optimized each image $i$ is divided into two orthogonal components. A force component parallel to the path $\hat{\tau}_i$ is the harmonic force between each image,

\begin{equation}
F_{i,\parallel} = k(|R_{i+1} - R_i| - |R_i - R_{i-1}|) \hat{\tau}_i
\end{equation}

where $k$ is the spring constant for the harmonic force. The orthogonal component to the pathway consists of the actual force acting on the system, from which the parallel projection is removed:

\begin{equation}
F_{i,\perp} = -\nabla E(R_i) + \nabla E(R_i) \cdot \hat{\tau}_i \hat{\tau}_i
\end{equation}

The total force used in the optimization is then the sum $F_i = F_{i,\parallel} + F_{i,\perp}$. Thus, the geometry is optimized orthogonal to the minimum energy path while along the pathway the spring force is minimized. An interpolated
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Figure 3.3. An illustration of a minimum energy path found for a two-dimensional potential $V(x, y) = \exp(-\cos(2\pi x) - \cos(\pi(y - x))) - \exp(-\cos(\pi y))$ from initial state $(0, 1)$ to final state $(1, 1)$. Each point on the line represents an image. The dark red line represents the interpolated initial guess and the bright red line the converged minimum energy path obtained using the CI-NEB method. The solution gives a saddle point with the value $(0.427, 0.777)$.

initial guess and an optimized MEP calculated using the NEB algorithm are illustrated in figure 3.3.

An improved variant developed by Henkelman et al.\textsuperscript{93}, dubbed the climbing image NEB or CI-NEB, defines the force differently for the image with the highest potential energy. For the highest energy image, the force parallel to the minimum energy path is therefore reversed:

$$F_{i,\text{max}} = -\nabla E(R_{i,\text{max}}) + 2\nabla E(R_{i,\text{max}}) \cdot \hat{r}_{i,\text{max}} \hat{r}_{i,\text{max}}$$

Thus, in the CI-NEB scheme the image with the highest potential energy starts to climb up the potential energy landscape along the minimum energy path and to approach the saddle point. Experience has shown that the climbing image NEB should be initiated only after the initial interpolated pathway has been sufficiently relaxed by normal NEB iterations to avoid the pathway from diverging.

3.2.5 Kinetic Monte Carlo

Kinetic Monte Carlo (kMC) is a stochastic simulation method that can be used to describe the time evolution of a chemical system. The kMC simulation consists of a sequence of discrete events, where the system jumps from different minimum energy structure to another. The probabilities for the different transitions are obtained from the reaction rates calculated from transition state theory.\textsuperscript{94,95}

The idea of first-principles kinetic Monte Carlo simulations is to combine the accurate atomic-scale description of the elementary processes
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and the statistical interplay between them in order to properly evaluate the kinetics of the surface chemistry. Simulating the kinetics of a heterogeneous system requires the evaluation of the statistical interplay within the manifold of elementary processes, most of which occur at very different time scales.\textsuperscript{94,95}

The chemical reactions are rare events in the sense that transitions between the initial and final states of the systems are separated by an energy barrier that first needs to be overcome. The probability of overcoming this barrier is exponentially dependent on the size of the barrier. Before and after a reaction, the system dwells within a PES basin in a random fashion before at some point jumping to another basin. The jump from one basin to another is thus completely independent of the preceding basins visited and hence the evolution of the process can be described as a Markov walk.\textsuperscript{94–96}

The principle of a kMC algorithm is as follows: given a starting configuration, the algorithm selects randomly an event from a set of possible events. The event is then executed and the system jumps to a new minimum energy configuration and the real time of the simulation is advanced by $\Delta t$:

$$t = t + \Delta t.$$  \hspace{1cm} (3.49)

There exists many possible events (e.g. adsorption, proton diffusion, ligand elimination reaction) for each given configuration. For each event there exists a Poisson probability distribution function that determines the time evolution. The system keeps track of the possible events for a given configuration in an event list. The rate constants $k_i$ for each event are determined using the transition state theory (eqn 3.41).

There exists many different algorithms to correctly describe the dynamics of the system.\textsuperscript{97–100} In the so-called first-reaction method\textsuperscript{98,99} the timestep for each process is determined by

$$\Delta t = \frac{\ln \rho_m}{k_m}.$$  \hspace{1cm} (3.50)

where $m$ is an index for a given event and $\rho_m$ is a random number generated from 0 to 1 for each possible event. The event with the shortest timestep is then chosen and executed and the event list is updated. This results in a correct mapping from the simulation events to the real time.

However, in this work the variable step size method (also known as the
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$n$-fold way) is used, originally presented by Bortz, Kalos and Lebowitz. The algorithm is summarized in figure 3.4. The BKL-procedure begins by calculating the total sum of rate constants for all the possible events available in the initial configuration,

$$k_{\text{tot}} = \sum_{i=1}^{N} k_i$$  (3.51)

Instead of generating a random number for each event, only two random numbers, $\rho_1$ and $\rho_2$, are generated. This greatly reduces the computational cost of the algorithm for large $N$. The first random number, $\rho_1$ is used to select the executed event. The algorithm selects the event $j$ that satisfies

$$\sum_{i=1}^{j-1} k_i \leq \rho_1 k_{\text{tot}} \leq \sum_{i=1}^{j} k_i$$  (3.52)

and executes it. After the event is executed, the event list is updated. Usually only few events in the list change and instead of searching through all the possible events and generating a new list at each step, the previous event list is preserved and updated for configuration $j$ and the sites affected by the event.

After the execution, the simulation time is advanced by

$$t = t - \frac{\ln(\rho_2)}{k_{\text{tot}}}$$.  (3.53)

The step size is independent of the executed event, but it does depend on the total sum $k_{\text{tot}}$ of the rate coefficients. This means that when fast events with large rate coefficients dominate the event list, the system clock advances very slowly.

In this work, an on-lattice kinetic Monte Carlo (kMC) was used to simulate the time evolution of the atomic layer deposition of zinc oxide. The chemical reactions of ZnO ALD via DEZ/H$_2$O are implemented into the Stochastic Parallel PARticle Kinetic Simulator (SPPARKS). The ALD-application in SPPARKS has been developed by Shirazi and Elliott and was used to study the ALD growth of HfO$_2$.

Our kinetic model is based on a set of mechanisms for the DEZ/H$_2$O ALD-process presented in publications II and III. The model follows the setup of Mahdi and Elliott and the mechanisms considered are divided into the following subsets: adsorption and desorption of the gaseous precursors, ligand elimination reactions between DEZ and surface oxygen.
Using coordination number and neighbor list, determine all possible events $N$ for a given configuration and construct a list. Calculate all reaction rate coefficients $k_i$.

Get two random numbers $\rho_1, \rho_2 \in [0, 1]$.

Calculate the total rate $k_{\text{tot}} = \sum_{i=1}^{N} k_i$. Use $\rho_1$ and find event $j$ so that $\sum_{i=1}^{j-1} k_i \leq \rho_1 k_{\text{tot}} \leq \sum_{i=1}^{j} k_i$.

Execute event $j$ and update event list by removing invalid events and adding new possible events.

Update clock of system using $\rho_2$, $t = t - \frac{\ln \rho_2}{k_{\text{tot}}}$.

Has time advanced sufficiently?

Yes  Stop

No

Figure 3.4. A flow-chart for the BKL-algorithm used in the kMC simulations.
Table 3.1. Different site types used in the model with descriptions. Each site type is assigned an integer and a corresponding string, where the X stands for the C\textsubscript{2}H\textsubscript{5} group.

<table>
<thead>
<tr>
<th>Enumeration</th>
<th>Type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>VACANCY</td>
<td>An empty site of no type</td>
</tr>
<tr>
<td>1</td>
<td>O</td>
<td>An oxygen atom</td>
</tr>
<tr>
<td>2</td>
<td>OH</td>
<td>A hydroxyl group</td>
</tr>
<tr>
<td>3</td>
<td>OH\textsubscript{2}</td>
<td>A surface water molecule</td>
</tr>
<tr>
<td>4</td>
<td>ZnX\textsubscript{2}O</td>
<td>Oxygen atom with an adsorbed DEZ molecule</td>
</tr>
<tr>
<td>5</td>
<td>ZnX\textsubscript{2}OH</td>
<td>Hydroxyl group with an adsorbed DEZ molecule</td>
</tr>
<tr>
<td>6</td>
<td>ZnX\textsubscript{2}OH\textsubscript{2}</td>
<td>Water molecule with an adsorbed DEZ molecule</td>
</tr>
<tr>
<td>7</td>
<td>ZnXO</td>
<td>Monoethylzinc on an oxygen atom</td>
</tr>
<tr>
<td>8</td>
<td>ZnXOH</td>
<td>Monoethylzinc on a hydroxyl group</td>
</tr>
<tr>
<td>9</td>
<td>ZnO</td>
<td>A zinc atom on an oxygen atom</td>
</tr>
<tr>
<td>10</td>
<td>ZnOH</td>
<td>A zinc atom on a hydroxyl group</td>
</tr>
<tr>
<td>11</td>
<td>Zn</td>
<td>A zinc atom</td>
</tr>
<tr>
<td>12</td>
<td>ZnX</td>
<td>A monoethylzinc group</td>
</tr>
<tr>
<td>13</td>
<td>OH\textsubscript{2}Zn</td>
<td>Water molecule adsorbed to a zinc atom</td>
</tr>
<tr>
<td>14</td>
<td>OH\textsubscript{2}ZnX</td>
<td>Water molecule adsorbed to a monoethylzinc group</td>
</tr>
<tr>
<td>15</td>
<td>OHZn</td>
<td>Hydroxyl group on a zinc atom</td>
</tr>
<tr>
<td>16</td>
<td>OHZnX</td>
<td>Hydroxyl group on a monoethylzinc group</td>
</tr>
<tr>
<td>17</td>
<td>OZn</td>
<td>Oxygen atom on a zinc atom</td>
</tr>
</tbody>
</table>

sites, ligand elimination reactions between MEZ and surface oxygen sites, proton diffusion between oxygen sites and densification of adsorbed Zn/O-containing fragments to the corresponding sublattices. The densification of the surface species is modified to be surface ligand-dependent.

Each lattice site is defined by its site number, type, coordination number (cn) and a neighbour list. The different site types are tabulated in table 3.1. The site types are enumerated i.e. each type is assigned an integer value to distinguish it from the other types.

The coordination number represents the number of covalent bonds a zinc/oxygen site has formed. The cn is the sum of the occupied first nearest neighbour sites and, in the case of a zinc lattice site, the cn also contains the number of ligands. Protons are not included in the coordination number.
The neighbour list contains the indices of the first neighbours of a given site. This list is used to navigate throughout the lattice network. No reference to the real space location is used in the model, the sites only react with respect to their nearest, or second nearest neighbours in the lattice. The type, coordination number and the neighbours of a given site are used to define what events are possible for that site.

For each site $i$, three event types are possible:

- **event I**: in this event, the type of a given site $i$ transforms to another type, e.g. in the adsorption of DEZ onto surface water:

  $$\text{OH}_2^{\text{site } i} \xrightarrow{\text{event I}} \text{ZnX}_2\text{OH}_2^{\text{site } i} \quad (3.54)$$

  Often the coordination number of the site is also updated. In this instance, the cn of the oxygen site is increased by 1 as a new Zn–O bond is formed.

- **event II**: a process between the site $i$ and the second nearest neighbour site $k$, e.g. a ligand-exchange reaction between the adsorbed DEZ and a surface hydroxyl group:

  $$\text{OH}^{\text{site } i} + \text{ZnX}_2\text{OH}_2^{\text{site } k} \xrightarrow{\text{event II}} \text{O}^{\text{site } i} + \text{ZnXOH}_2^{\text{site } k} \quad (3.55)$$

  The proton of the hydroxyl group and the ethyl-ligands from diethylzinc combine to form an ethane molecule that readily desorbs from the surface. The cn of either site is not affected by the reaction. The protons do not contribute to the cn of the OH site and the bonding of the oxygen on the ZnX2OH2/ZnXOH2 site, that resides on the oxygen sublattice, is not changed. In general, the types on both sites $i$ and $k$ need not change in an event II process.

- **event III**: the event is described as a process between the site $i$ and the first nearest neighbour site $j$, e.g. a densification process (see publication IV for more details) where a ZnX group moves from the oxygen site to a vacant site on the metal sublattice:

  $$\text{VAC}^{\text{site } i} + \text{ZnXOH}_2^{\text{site } j} \xrightarrow{\text{event III}} \text{ZnX}^{\text{site } i} + \text{OH}_2^{\text{site } j} \quad (3.56)$$

  Coordination numbers of each site participating in the event as well as
Figure 3.5. A schematic illustration of the lattice structure used in for the model. The metal and oxygen sites alternate in the lattice (metal sites are coloured by light grey, oxygen sites with light red). Each site is defined by its location in the lattice, type and coordination number. The coordination number is shown below each lattice box. The bottom row in the figure is the bulk-phase (Zn with cn 4). The bulk is inert i.e. no process is defined for sites with cn 4. Initially the surface is covered with low-coordinated hydroxyl groups. Above the surface is the gas-phase that is initially filled with vacant (VAC) lattice sites. As the deposition process continues, the simulation produces a crystalline ZnO lattice with some lattice defects.

The model takes a crystalline wurtzite zinc oxide structure as an input. Since the lattice structure is preset in our simulation, we cannot determine whether an amorphous film grows or which crystal phase is obtained. The cation-anion sites alternate within the metal oxide lattice, dividing the lattice naturally into metal and oxygen sublattices. This alternation of cation and anion sites makes the implementation of different reaction mechanisms simple, since the first nearest neighbour of each metal site belongs to the oxygen sublattice and the second nearest neighbour belongs again to the metal sublattice. As only charge neutral species are introduced/removed from the system during the simulation, the charge balance is preserved in the simulation.

The distinguishing feature of an atomic layer deposition process is the separation of the reactants into two gas pulses divided by a purging of the reactor chamber. This is implemented in our model by a time-dependent variable that switches the adsorption of DEZ and H₂O on and off during the simulation. This variable only effects the adsorption processes as all other surface processes are allowed to be executed throughout the simula-
The length of each pulse/purge can be defined separately. A default length of 50 ms was set for pulses and purges in the simulations.

Results from the kinetic simulation are presented in chapter 4.3. The mechanisms implemented in the model as well as further details on the results are discussed in publication IV.
Theoretical Methods
4. Results and Discussion

Computational chemistry is a powerful tool for studying atomic level phenomena. By studying the elementary surface reactions that transform the precursor molecules into the product film and identifying the crucial steps, the overall growth process can be understood.

Computational studies on the surface reactions of ALD have usually used either a gas-phase cluster or a periodic surface slab model. In the cluster-model the surface is represented by a atomic cluster in vacuum with one or more reactive sites are present. Due to the simplicity of the model, these type of simulations are inexpensive to conduct. However, neglecting the entire surface can have unpredictable consequences and it is not clear how much the electronic structure of the cluster differs from the actual surface and how this will affect the results. Many of the early computational publications\textsuperscript{38,103} on the surface reactions used the cluster-model but the approach is still often employed\textsuperscript{43,44}.

In this work the atomic layer deposition of aluminium and zinc oxides have been investigated using density functional theory. Activation energies for both precursor pulses were calculated using a periodic surface model. These activation energies can be used to interpret the progression of the deposition process.

In the case of zinc oxide, the reaction barriers were implemented into a kinetic model to produce a time-dependent model of the process. A kinetic model is the ultimate test for a computational simulation; if the model does not sufficiently reproduce the macroscopic process, the set of reactions must be incomplete. However, due to the nonlinearity of the process, one cannot state with certainty that a model is complete if there is one-to-one correspondence with measurements.
Here the main results of the thesis are discussed. The publication I focuses on the ALD of $\text{Al}_2\text{O}_3$ via TMA/$\text{H}_2\text{O}$-process. Publications II-III consider the surface chemistry of the DEZ/$\text{H}_2\text{O}$-process. In publication IV, the calculations for the DEZ/$\text{H}_2\text{O}$-process are implemented into a kinetic model where the macroscopic growth of the thin film is simulated.

4.1 Surface reactions during $\text{Al}_2\text{O}_3$ ALD

Surface reactions during the ALD of $\text{Al}_2\text{O}_3$ using TMA and water as precursors has previously been studied by Widjaja and Musgrave, Elliott and Greer and Elliott and Pinto. Elliott, Greer and Pinto used an explicit surface slab model in their simulations. The hydroxylation of the surface was achieved by substituting the top-most aluminium oxide layer with aluminium hydroxide, gibbsite. The gibbsite-covered surface is the most thermodynamically stable configuration at 0 K.

However, the gibbsite surface is not thermodynamically stable at the process conditions but the surface is covered with dissociatively adsorbed water molecules. In publication I we compared the differences on the surface reactions between the two cases, a gibbsite surface and hydroxylated surface. The two hydroxylated surfaces are depicted in figure 4.1. A (0001) $\alpha$-$\text{Al}_2\text{O}_3$ was used as a starting point for both surfaces. The surface reactions for both the trimethylaluminium and water were investigated.

The gibbsite-like surface is constructed by replacing the surface Al-atoms with three hydrogen atoms. This turns the top-most layer into aluminium hydroxide, $\text{Al}_2\text{O}_3 \longrightarrow \text{Al(OH)}_3$, with two of the hydroxyl groups being oriented vertically and one horizontally with respect to the surface. The adsorption of TMA is preferred onto the horizontal hydroxyl group.
The hydroxylated water surface is constructed by adding dissociated water molecules onto a bare Al₂O₃ surface. The dissociation of water leads to two kinds of hydroxyl groups, the water molecule fragment being higher on the surface than the one formed from a surface oxygen. This changes the geometry of the surface when compared to the gibbsite model used by Elliott and Greer⁴⁰: only the top most hydroxyl group is accessible for TMA, while on the planar gibbsite surface difference between various sites is smaller.

TMA was found to adsorb exothermically onto the hydroxylated surface with a strong adsorption bond of -1.13 eV. The ligand elimination reaction with the surface hydroxyl group, converting TMA into DMA, was found to have a low barrier of 0.35 eV. The adsorption energy of TMA was found to depend on the surface TMA/DMA coverage. The TMA and DMA were able to form methyl-bridges between one another, stabilizing the adsorption configuration and increasing the adsorption energy of TMA. However, the increased stabilization also increased the activation energy for the ligand elimination reaction for TMA. The barrier increased to 0.71 eV at high DMA+TMA concentrations.

The removal of the second ligand was also found to have a low barrier, 0.51 eV. However, elimination of the final ligand from MMA had a high barrier (1.05 eV) due to the three-coordinated structure.

In comparison with the previously used gibbsite-like surface, the activation energy for the removal of the first methyl-ligand was calculated to be 0.69 eV, slightly lower than reported in ref 41. The barrier for the removal of the second ligand on the gibbsite-like surface remained higher, 0.72 eV. Thus, the chosen surface model has large effect on the energetics of the surface calculations.

At the process conditions (450 K temperature) the relative magnitudes for the reaction rate coefficients for the removal of the first, second and third ligands, based on calculations on the hydroxylated surface presented in publication I, are $10^9 : 10^8 : 10^2$, respectively. From the rates, it can be concluded that TMA rapidly converts to MMA on the surface. While the removal of the final ligand is possible, it is unlikely to contribute much to the overall growth as most of the hydrogen on the surface is likely consumed by the first two reactions. The TMA pulse then leads to a composition of DMA and MMA fragmentns on the surface.
Results and Discussion

After the TMA pulse, the reactor chamber is purged with nitrogen and water is introduced into the system. The water pulse reactions were studied on isolated DMA and MMA fragments on the surface. For an isolated DMA, the barriers for the removal of the methyl ligands were calculated to be relatively low, ranging from 0.44 eV to 0.67 eV. The MMA, however, is inaccessible to a direct attack by a water molecule. A complex mechanism was found, containing several water molecules. The 3-coordinated structure of the MMA was first broken by one water molecule and the methyl was removed by a second water molecule, demonstrating that the removal of the methyl from an MMA requires water–water cooperation.

Shirazi and Elliott\textsuperscript{42} observed that TMA fragments on the surface can catalyze the ligand-exchange reactions. This leads to a decreasing trend in the ligand-exchange barriers as the surface methyl-concentration increases, observed experimentally by Vandalon and Kessels.\textsuperscript{25} In our calculations, the barrier for a ligand-exchange between water and DMA or MMA-OH increases from 0.44 eV to 0.67 eV. This increase is in qualitative agreement with experimental data\textsuperscript{20}, where the removal of the first methyl-ligand from DMA is observed faster than the removal of the second ligand. However, the overall methyl-coverage in our the simulations is low and it is difficult to comment on the effect the surface methyl-coverage may have on the energetics on the hydroxylated surface.

In addition to the $\alpha$-$\text{Al}_2\text{O}_3$, the TMA/H$_2$O-process surface chemistry has also been studied on $\gamma$-$\text{Al}_2\text{O}_3$ surface by Sandupatla \textit{et al.}\textsuperscript{105}. The authors report a higher activation energy of 0.80 eV for adsorbed TMA reacting with a surface water molecule. The activation energy calculated for DMA was lower (0.68 eV) than that for TMA. The MMA has a considerably higher barrier of 1.64 eV. Overall, these finding are in agreement with those presented in this work. While the barriers for TMA and DMA reported by Sandupatla \textit{et al.} are somewhat larger than those presented in this work, they are still accessible in the process conditions. The inertness of MMA is confirmed in both cases.

For the water pulse reactions, the authors observe an increasing trend in the activation energy going from TMA to MMA, ranging from 0.77 to 1.61 eV. This data is difficult to compare with the results in publication I as TMA–H$_2$O reaction was not studied, as all TMA is assumed to convert to DMA. Both the work done in this thesis as well as the work by Sandupatla
et al. agree that the MMA is basically inert to an attack by a single water molecule. However, the cooperative effect of several water molecules was not investigated by Sandupatla et al.

The surface reactions of TMA were also studied by Delabie et al. on Si- and Ge-clusters. The authors observed an overall trend of increasing activation energy for methyl-elimination from TMA to MMA. The activation energy for TMA ranged from 0.48 to 0.65 eV, for DMA from 0.93 to 1.09 eV and for MMA from 1.21 to 1.56 eV, depending on the cluster. These findings are in agreement with the results of publication I, where the initial kinetics of TMA are rapid and the end product of the TMA adsorption is MMA.

4.2 Surface reactions during ZnO ALD

Publications II-III focus on the deposition of ZnO using diethylzinc and water. Zinc oxide thin films have various applications. The initial goal of the thesis was to study the deposition of so-called organic–inorganic hybrid thin films. Hybrid thin films containing zinc oxide, zincones, have shown promise in the recent years. However, in order to study the adsorption and surface reactions for the organic precursors, a sufficient model for the DEZ saturated surface is needed and the overall process of DEZ/H₂O must be understood.

The DEZ/H₂O-process is similar to the TMA/H₂O-process in that the precursors react rapidly with each other and the reaction by-product is inert, relatively small molecule, ethane. However, since the metal-precursor only has two ligands, the metal precursor has only two possible surface-fragments: monoethylzinc and bare zinc. Most of the computational studies on ALD focus on the initial stages of the deposition when the precursor coverage is low. Since DEZ only has two possible surface fragments, it is possible to produce reasonable estimates for surface structures saturated with the metal-precursor and to study the effects thereof. The surface reactions and surface saturation of diethylzinc is the focus of publication II and the reaction mechanisms during the subsequent water pulse on ethyl-saturated surface are considered in publication III.

A nonpolar (100) lattice orientation was used to model the zinc oxide
surface. This orientation is the dominant orientation within the temperature range of 160-200°C, corresponding roughly to the ALD window of the process.\textsuperscript{31–33} The hydroxylation of the surface by water molecules has been well established both experimentally and theoretically.\textsuperscript{107–109} When the planar (100) surface is hydroxylated, water forms a $2 \times 1$ periodic network of dissociated and associated water molecules hydrogen bonded to each other via hydrogen bonds.

In addition to a planar surface, two hydroxylated surfaces with a step were constructed to compare the difference between an ideally crystalline surface and a nonideal step. The steps were created by cleaving the topmost oxide layer along the (010) and (001) lattice orientations as illustrated in figure 4.2. The excess strain from the step structure was removed by running an \textit{ab initio} molecular dynamics simulation. Snapshots from the trajectory were optimised and the minimum energy structures were used for the DEZ surface reactions. The step surfaces were hydroxylated by placing water molecules onto the surface zinc atoms.

The DEZ is a Lewis-acid and prefers to form an adsorption bond with the lone pair of a surface oxygen. The adsorption energy of DEZ onto a surface hydroxyl group or water molecule was calculated to be exothermic in all cases. The planar surface contained both hydroxyl and water groups and the preferred adsorption site was onto the water molecule with adsorption energy of -0.74 eV. Adsorption energies on the stepped surface were -0.64 eV and -1.19 eV.
For the diethylzinc adsorption to be irreversible, it has to lose one of its ligands. The ethyl-ligand is eliminated via ligand-exchange with a surface hydroxyl group. The ethyl accepts a proton resulting in an inert ethane-molecule and a monoethylzinc surface fragment. On the planar surface the barrier for the removal of the first ligand was calculated to be 0.23-0.47 eV, depending on the surface ethyl-coverage. However, on the step surfaces this barrier was considerably higher, 0.9 eV. After the ethane is formed, it irreversibly desorbs to the gas-phase.

The monoethylzinc may react further with a surface hydroxyl group or a water molecule. However, this reaction was calculated to have a high barrier in all cases. The calculated barriers ranged from 1.31 eV to 1.52 eV on the planar surface and from 0.95 eV to 1.59 eV on the step surfaces. Processes with activation energies above 1 eV are very slow at the deposition conditions, so most of the mechanisms found can be ruled out as not occurring during deposition. However, if one considers the lowest calculated barrier of 0.95 eV to be representative, the second ligand may be removed at some instances at elevated deposition temperatures.

In addition to ligand-exchange reactions, the pyrolysis of diethylzinc was also investigated as a possible reaction pathway as suggested in the literature. However, based on our calculations the barrier for pyrolysis on the surface is close to 2 eV and is therefore not expected to contribute to the deposition of the film.

Based on the relative kinetics of the ligand-elimination reactions, two saturated surface structured were constructed. First, a low temperature estimate, labelled case 1 structure, was built on the assumption that at low deposition temperatures only one ethyl-ligand was removed from DEZ during adsorption. The surface would then be covered with monoethylzinc and the limiting factor would be the steric repulsion between the surface ethyl-ligands. Second, a high temperature estimate, labelled case 2 structure, was constructed assuming that both the ethyl-ligands can be eliminated at elevated temperatures. The limiting factor would then become the amount of hydrogen on the surface as well as steric repulsion between the surface fragments. The two saturated surface structures are illustrated in figure 4.3.

The relative deposition rates were estimated using these saturated structures. Assuming that all the ethyl-ligands were removed from the surface
Results and Discussion

Figure 4.3. Two diethylzinc saturated surface structures constructed in publication II and used in publication III. The case 1 structure (left) is an estimate for the DEZ saturated surface at low deposition temperatures. The case 2 structure (right) represents saturated surface at high deposition temperature range.

during the water pulse and replaced with OH-groups, the low and high temperature estimates would correspond with growth per cycles of 1.7 and 2.1 Å, respectively, in good agreement the experimental data. However, estimating the deposition rates in this manner is an oversimplification, as it has since been shown by Mackus et al.\textsuperscript{35} that removal of the ethyl-ligands during the water pulse is in fact incomplete. This persistence of the surface ethyl-ligands is supported by our calculations presented in publication III.

In publication III, the elementary surface reactions for the water pulse were studied. \textit{Ab initio} surface chemistry is usually studied isolated reactive sites in order to simplify the surface environment. Initially, we looked at the adsorption of a single water molecule onto an isolated monoethylzinc fragment on the planar surface. However, the barrier for the ligand-exchange reaction between a single monoethylzinc and a water molecule is relatively large (0.96 eV). Surface fragments have previously\textsuperscript{42} been shown to lower the activation energy for ligand-exchange during the water pulse, so to further investigate this, the water pulse calculations carried out on both case 1 and case 2 saturated structures.

Because of the presence of ethyl-ligands on the surface, the saturated structures contain vast number of additional degrees of freedom. Unlike for a crystalline ZnO (100) surface, the minimum energy structure of a saturated surface is not well defined. To overcome this complexity, \textit{ab initio} molecular dynamics (AIMD) was employed to sample possible con-
Results and Discussion

Figure 4.4. The growth-per-cycle (GPC) as a function of temperature interpreted using the DFT calculations from publication III. The measurement points are adopted from ref 12. Different symbols (empty squares, empty circles, black circles) correspond to different experimental runs. The LE1 and LE2 correspond to the DEZ and MEZ ligand elimination reactions on the surface leading to MEZ and Zn, respectively. Case 1 and case 2 are the low and high temperature ethyl-saturated structures, respectively, discussed in publication II.

figurations. After a water molecule was introduced into the system, an AIMD simulation was carried out so that the system could freely explore the potential energy surface. Snapshots from the trajectory were then optimised and the lowest energy configuration was chosen as the starting point for a ligand elimination reaction. This provided a set of activation energies for ligand elimination reactions on the surface at various ethyl-concentrations.

Water adsorbs very exothermically on the saturated surface at all ethyl-coverages. This is in stark contrast to the calculations on the isolated monoethylzinc, where water formed only a weak adsorption bond with the monoethylzinc, with bond energy of only -0.36 eV. There exists then a cooperative effect, whereby the monoethylzinc increase the adsorption energy of water. However, we observed only a weak cooperative effects for the ligand elimination barriers. No strong dependency between the activation energies and surface ethyl-concentration was observed. The activation energies ranged from 0.72 eV to 1.56 eV, with all but one residing above 0.9 eV and most above 1 eV.

Since most of the computed barriers are large and the only low barrier
Our findings are summarized in figure 4.4, where the kinetic data is used to interpret the temperature dependency of the thin film growth. Because the removal of the first ligand from DEZ has a low barrier, the surface becomes saturated with MEZ at all temperatures. This corresponds roughly to the case 1 of our ethyl-saturated structures presented in publication II. Because of the large kinetic barrier for the removal of the ethyl-ligands, the thin film grows poorly at low temperatures. At some threshold, the removal of ethyl-ligands becomes feasible and the film starts to grow.

At elevated temperatures, some of the MEZ may react further to Zn (LE2) during the DEZ pulse. This decreases the steric repulsion between zinc precursor molecules and increases DEZ adsorption. This also creates further sites for water to adsorb to and increases the GPC. This corresponds to the case 2 ethyl-saturated surface where the saturation is limited by the amount of available protons on the surface as well as the steric repulsion between the ligands. At very high temperatures, desorption of the precursors starts to dominate, leading to a decrease in the overall GPC.

4.3 ZnO ALD growth process

Most of the computational work done on the atomic layer deposition has focused on the study of different surface mechanisms during the deposition. Comparing the activation energies of selected key reaction steps may give an adequate description of the overall process. However, the validity of the calculations can only be estimated by mapping the calculated mechanisms onto macroscopic scales using a kinetic model. Evaluating the overall growth process is difficult due to the complex interplay of the surface reactions.

To properly account for the complex surface environment present during
deposition, a lattice-based kinetic Monte Carlo method was used to simulate the overall growth of the zinc oxide thin film. The density functional theory calculations provide a set of reaction pathways that can be used to construct a network of events to describe a deposition cycle. The kMC algorithm is used to generate an ensemble of trajectories and the correct dynamics are obtained by averaging over the entire ensemble.\textsuperscript{94,95}

4.3.1 The kinetic Monte Carlo model

The kinetic Monte Carlo used in publication IV is based on an ALD-application developed by Shirazi and Elliott\textsuperscript{51}. Shirazi and Elliott have previously used the application to study the ALD growth of HfO\textsubscript{2} from first principles. The application is part of the Stochastic Parallel PARticle Kinetic Simulator (SPPARKS)\textsuperscript{101,102} package, written in C++. To learn how to use and develop the program to model the zinc oxide ALD, I visited the Tyndall institute in Cork, Ireland for a short-term scientific mission (STSM) funded by the HERALD (Hooking together European research in Atomic Layer Deposition)\textsuperscript{110} organization.

The kMC model follows the setup of Mahdi and Elliott\textsuperscript{51}. The mechanisms included in the model can be divided to the following subsets: adsorption and desorption of the gaseous precursors, ligand-exchange reactions between DEZ and surface oxygen sites, ligand-exchange reactions between MEZ and surface oxygen sites, proton diffusion between oxygen sites and densification of adsorbed Zn/O-containing fragments to the corresponding sublattices.

The kMC model is an on-lattice model where the wurtzite lattice structure of zinc oxide\textsuperscript{111} is given as an input and in the course of the simulation a ZnO lattice is reproduced. Each lattice site in the framework represents an atom or a molecule. A ZnO (100) surface facet covered with water molecules is used as the initial state of the simulation.

The state to state evolution of the system is propagated by the Bortz–Kalos–Lebowitz algorithm\textsuperscript{97}. Activation energies used to compute the rate constants were adopted from density functional theory calculations presented in publication II and III. The implementation of the model is discussed in publication IV and only the main results of the model are discussed here.
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Figure 4.5. The simulated QCM data from the kMC model. Initially the growth rate is the same for at all temperatures when the surface becomes saturated with DEZ. However, after ethyl-saturation the different temperature graphs diverge as the elimination of ethyl-ligands is low at low temperatures.

4.3.2 Mass increment

The dynamical simulation enables a direct comparison with various experimental methods. A quartz-crystal microbalance is commonly used in ALD experiments to measure the change in the mass of the deposited thin film as a function of time. A similar time-dependent data on the mass of the film can easily be extracted from the kinetic simulation by calculating the molecular mass of each site on the lattice as the simulation progresses. An example of such a mass-gain graph for the deposition at various temperatures is depicted in figure 4.5.

Each simulation consists of a DEZ/purge/H₂O/purge sequence, each lasting for 0.05 seconds. The total simulation consists of 10 full ALD cycles in 2 seconds. The different ALD cycles can be identified from the step-like shape of the mass–time graph. The initial DEZ saturation is almost identical at all temperatures in the first ALD cycle, because the initial surface is clean of ethyl-ligands and reactions for DEZ have a low barrier.

After the first cycle, however, there is a clear divergence in the simulated QCM graphs depending on the deposition temperature. At low temperatures, where the growth of the thin film is poor, the graph flattens out after the first two ALD cycles. At elevated temperatures, the mass-gain is
Results and Discussion

Figure 4.6. The simulated mass-change as a function of time from the kMC model (left) and the corresponding experimental QCM measurement adopted from ref 112 (right). The different phases (DEZ pulse/purge/H2O pulse/purge) within the ALD cycle are indicated by the vertical dashed lines. The ZnO thin films were deposited at temperature 177 °C, in both the simulation and the experiment. The deposited mass is overestimated in the simulation, but the simulation is in qualitative agreement with the experimental data. The reader should note the order of magnitude difference in the deposition timescales between simulation and experiment.

identical from each ALD cycle to next.

For a direct comparison with an experimental112 QCM graph of a single representative ALD cycle, the simulated QCM data was averaged over the final 8 ALD cycles. The experimental and simulated QCM graphs are plotted in figure 4.6. Both the simulations and the experiment were conducted at 177 °C. The graphs are in good qualitative agreement with one another. The main mass-gain comes from the DEZ pulse and the mass–time graph reaches a saturation. The water pulse initially causes a small mass-gain that slowly decreases and reaches a steady level.

The simulated graph is stable during the purge phases, for both DEZ and H2O, but in the experimental graph there is a significant decrease in the deposited mass for both reactants. This is likely due to weakly bounded precursors and by-products desorbing from the surface. No such effect is observed in the simulation since no weakly bound species are present during the DEZ pulse and ethane desorption is assumed to be instantaneous.

4.3.3 Thickness increment

The average thickness increment of the deposited thin film is commonly used in experiments to evaluate the growth of the thin film. This in-
crement is usually expressed in growth per cycle (GPC), the change in thickness of the film after a full ALD cycle.

The growth per cycle of the simulated thin film can be estimated in various ways. One way is to calculate the average mass deposited onto the surface area from the slope of the mass–time curve in figure 4.5. Dividing this average mass per area with the density of the bulk ZnO (5.62 g cm$^{-3}$), the growth-per-cycle can be calculated in the same fashion as done in an experimental QCM measurement$^{12}$.

The average growth per cycle can also be obtained by dividing the change in thickness of the simulated thin film with the number of ALD cycles. However, the height of the simulated film is not well defined since the film does not grow entirely uniformly, at least at low temperatures. We have defined the "top" of the thin film as the layer in which 50 % or more of the lattice sites have been occupied by either zinc or oxygen species. The GPC calculated this way was found to be robust and can be reproduced with higher cutoffs of 60 % and 80 %. The GPC with respect to temperature from our simulations is presented in figure 4.7 alongside with experimental data by Yousfi et al. from ref 12.

The two different approaches for estimating the growth per cycle from the simulation converge nicely and agree with the experimental data. At low temperatures the growth of the thin film is slow. This is due to the high activation energy required for eliminating the surface ethyl-ligands. At temperature 50 °C and above is the actual onset of thin film growth, in qualitative agreement with experiment. The simulated GPC increases more rapidly as a function of temperature than is observed experimentally. The GPC reaches a plateau after 125 °C, the so-called "ALD window", where the GPC stable with respect to the temperature.

Quantitative error at maximum growth between the simulation and experiment is 16 %. The GPC reported by Yousfi et al.$^{12}$ is somewhat larger than in other experimental publications where the thickness of the film is calculated in some different fashion. However, a QCM measurement best relates to our simulation.

The good agreement with the experimental QCM data on the onset of thin film growth is somewhat surprising, since the GPC is very sensitive to the barriers for the elimination of the monoethylzinc. The sensitivity of the simulation is illustrated in figure 4.8 where the barriers for the elim-
Results and Discussion

Figure 4.7. Simulated growth per cycle, estimated from both the thickness of the simulated thin film and from the deposited mass, compared to the GPC reported in ref 12. The GPC estimated from the average mass includes the error bars, obtained as a standard deviation from series of simulations. The simulated data is in excellent qualitative agreement with the experimental data, correctly predicting the onset of the film growth. Quantitative error between simulation and experiment at maximal growth rate is 16%.

The reaction with the lowest barrier in our model is a mechanism between a monoethylzinc and a singly coordinated water molecule. This is the dominant mechanism for eliminating the monoethylzinc at low temperatures. After 100 °C, the mechanisms involving hydroxyl groups also become accessible.

The slow deposition of ZnO at low temperatures is the result of poor elimination of the ethyl ligands from the surface during the water pulse.
Results and Discussion

Figure 4.8. Growth-per-cycle as a function of temperature in the case where the second ligand-exchange reaction (LE2) has been increased/decreased by 0.10 eV. Increasing the barrier shifts the slope of the GPC-curve to the right as the ligand-elimination reaction can occur only at elevated temperatures. Decreasing the barrier shifts the slope to left.

After the water pulse, the surface remains covered with ethyl-ligands and the adsorption of DEZ in the subsequent ALD cycles is inhibited due to steric interactions between the ligands. At elevated temperatures, more and more ethyl-ligands are removed, leading to an increase in $\text{H}_2\text{O}$ and DEZ adsorption and to an increase in the overall deposited mass.

The incomplete elimination of the ethyl-ligands leads to ligands persisting on the surface after the water pulse. These ligands are not eliminated from the system because of the large activation energy. A fraction of the newly deposited ligands that persist on the surface after each cycle can be computed from the simulation. We defined fraction of persisting ligands, $f_{\text{ethyl}}$ as

$$f_{\text{ethyl}} = \frac{\Delta N_{\text{ethyl, DEZ+H}_2\text{O}}}{\Delta N_{\text{ethyl, DEZ}}}$$  (4.1)

where $\Delta N_{\text{ethyl, DEZ}}$ is the change in the total number of ethyl ligands after the DEZ pulse and $\Delta N_{\text{ethyl, DEZ+H}_2\text{O}}$ is the change in the total number of ethyl ligands after both DEZ and $\text{H}_2\text{O}$ pulses. The fraction then roughly corresponds to the fraction of the newly deposited ligands that remain on the surface at the end of the cycle.

$f_{\text{ethyl}}$ as a function of temperature is plotted in figure 4.9 alongside with experimental data on the fraction of persisting ligands. $f_{\text{ethyl}}$ is calculated...
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**Figure 4.9.** The fraction of persisting ligands as a function of temperature in the simulation. Experimental data obtained from ref 35, corresponding to low and high water exposures.

as an average over the last 8 ALD cycles. The experimental data on the fraction of persisting ligands has been calculated from a measured difference FTIR spectra after a DEZ/H$_2$O cycle. The ZnO surface was prepared in the experiments by cleaning it with H$_2$O at 300 °C before the measurement.

The simulation is in qualitative agreement with the limited experimental data available. The removal of the monoethylzinc is clearly very sensitive to temperature. The incomplete elimination of the ethyl-ligands is clearly the main reason for the low GPC at low temperatures as no further zinc can deposit onto the ethyl-saturated surface. In our kMC model the fraction of persisting ligands reaches a limit of 45 % ligands persisting after each ALD cycle, while experimentally it is observed that the fraction decreases close to zero at elevated temperatures. It is likely that a yet unidentified process, for example, a transfer of $\beta$-hydride and desorption of C$_2$H$_4$, is responsible for the elimination of ethyl from the surface / lattice.
4.4 Reliability of the findings

How stable are the results obtained in the thesis? To evaluate the robustness of the results, some calculations with different approximate density functionals were conducted for comparison. Calculations on the reaction pathways were done as single point on the reaction pathways obtained using the PBE-functional and calculations for the adsorption structures were optimized. No hybrid functionals were used due to the poor implementation of the exact exchange in GPAW.

The activation energies for the first ligand-exchange reactions in TMA/H₂O and DEZ/H₂O processes are presented in table 4.1. The LDA clearly underestimates the barrier compared to the GGA functionals, a phenomenon well documented in the literature. However, the barriers calculated using different LDA/GGA functionals are in good agreement with each other and seem to be rather stable.

Similar data set for adsorption energies is presented in table 4.2. For the adsorption energies, all the configurations were optimised. Adsorption energies are known to be difficult to quantitatively estimate with DFT.⁶⁹,¹¹³,¹¹⁴ The well known overbinding of the LDA functional is evident in the adsorption energies when compared to the GGA functionals. The pure PBE and its variants predict no bond between a DEZ and the ZnO surface. Inclusion of the dispersion interaction increases the bonding of the precursor (for both PBE+vdW and BEEF-vdW) and gives a moderate adsorption energy for DEZ.

There is no experimental data available on the DEZ adsorption to the zinc oxide surface, but adsorption energy benchmarks for several functionals are available for metal and metal oxides surfaces.¹¹⁴,¹¹⁵ For weakly adsorbed molecules, where the dispersion interaction likely has a large contribution, PBE and RPBE underestimate the adsorption energy while BEEF-vdW provides systematically better estimates. The zero adsorption energy estimated for DEZ by PBE, RPBE and revPBE is likely due to presence of the large ethyl-ligands. Due to the poor description of the weak van der Waals interaction⁷⁶ by these functionals, the interaction between the ethyl-ligands and the surface remains purely repulsive, leading to a non-bonding DEZ. Inclusion of the dispersion interaction decreases this repulsion and leads to the formation of an adsorption bond. In line with
### Table 4.1. Calculated activation energies for the initial surface reaction in publications I-III.

<table>
<thead>
<tr>
<th>Functional</th>
<th>$E_a / \text{eV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>PBE+TS09</td>
<td>0.35</td>
</tr>
<tr>
<td>LDA</td>
<td>0.20</td>
</tr>
<tr>
<td>RPBE</td>
<td>0.41</td>
</tr>
<tr>
<td>revPBE</td>
<td>0.40</td>
</tr>
<tr>
<td>BEEF-vdW</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>PBE</td>
<td>0.52</td>
</tr>
<tr>
<td>PBE+TS09</td>
<td>0.47</td>
</tr>
<tr>
<td>LDA</td>
<td>0.39</td>
</tr>
<tr>
<td>RPBE</td>
<td>0.59</td>
</tr>
<tr>
<td>revPBE</td>
<td>0.58</td>
</tr>
<tr>
<td>BEEF-vdW</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>PBE</td>
<td>1.16</td>
</tr>
<tr>
<td>PBE+TS09</td>
<td>1.15</td>
</tr>
<tr>
<td>LDA</td>
<td>0.99</td>
</tr>
<tr>
<td>RPBE</td>
<td>1.23</td>
</tr>
<tr>
<td>revPBE</td>
<td>1.21</td>
</tr>
<tr>
<td>BEEF-vdW</td>
<td>1.25</td>
</tr>
</tbody>
</table>

### Table 4.2. Calculated adsorption energies for the initial surface reaction in publications I-III.

<table>
<thead>
<tr>
<th>Functional</th>
<th>$E_{ads} / \text{eV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>PBE+TS09</td>
<td>-0.65</td>
</tr>
<tr>
<td>LDA</td>
<td>-1.18</td>
</tr>
<tr>
<td>RPBE</td>
<td>-0.39</td>
</tr>
<tr>
<td>revPBE</td>
<td>-0.34</td>
</tr>
<tr>
<td>BEEF-vdW</td>
<td>-0.85</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>PBE</td>
<td>-0.05</td>
</tr>
<tr>
<td>PBE+TS09</td>
<td>-0.70</td>
</tr>
<tr>
<td>LDA</td>
<td>-0.72</td>
</tr>
<tr>
<td>RPBE</td>
<td>0.05</td>
</tr>
<tr>
<td>revPBE</td>
<td>0.05</td>
</tr>
<tr>
<td>BEEF-vdW</td>
<td>-0.42</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>PBE</td>
<td>-0.96</td>
</tr>
<tr>
<td>PBE+TS09</td>
<td>-1.20</td>
</tr>
<tr>
<td>LDA</td>
<td>-1.50</td>
</tr>
<tr>
<td>RPBE</td>
<td>-0.69</td>
</tr>
<tr>
<td>revPBE</td>
<td>-0.64</td>
</tr>
<tr>
<td>BEEF-vdW</td>
<td>-0.96</td>
</tr>
</tbody>
</table>
the benchmark results, the van der Waals interaction is not as significant in the case of water adsorption where all the functionals predict rather strong (although varied) adsorption energies for water.

It is a well known phenomenon that, due to the over delocalization of the electron density in an approximate density functional, the activation barriers calculated using DFT are consistently underestimated. A hybrid functional could be used to improve the accuracy of the barriers but with a computational cost.

However, an error in the opposite direction may occur in the way the transition states are calculated. While the CI-NEB is a robust procedure for searching saddle points on the potential energy surface, it is possible that not all degrees of freedom are sufficiently relaxed, as they would be if, say, a full Hessian-matrix procedure had been used. The transition states were not checked with vibrational mode analysis as there is a lot of noise in the vibrational modes calculated using GPAW. It is possible therefore, that an activation energy calculated using the CI-NEB method slightly overestimates the transition barrier within the DFT framework. However, as the barriers were obtained from well converged minimum energy pathways and many calculations were conducted for different reaction mechanisms with barriers of similar mechanisms supporting each other, the error on the reported barriers is likely to be small.

Whether or not the barriers are accurate in the absolute values is not detrimental to the overall thesis, however, as the relative size of the barriers of different reactions is more important. If all the barriers are underestimated, the kinetics of the process are estimated to be too fast but the execution of the events should be in the correct order.

### 4.5 Future Work

Density functional theory has proven to be a valuable tool for understanding the molecular level phenomena during an atomic layer deposition process. DFT can be used to further our understanding of a known ALD process or as a problem-solving tool in collaboration with experimental research in search for novel processes. However, one should always remember to try to map the computed barriers onto the macroscopic scale.
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of the overall process to confirm the validity of the calculations and the model.

Predicting the growth rate from atomic scale calculations is time consuming, especially if working with a novel process. The often used cluster-model calculations are computationally cheap and a large amounts of molecules may be explored in a short time. However, it is by no means obvious how the activation energies calculated using a cluster-model actually relate to the growth of the thin film as there seems to be discrepancies between the cluster-model calculations and a more realistic surface-model calculations. I consider the use of a surface slab model a necessity unless the reliability of a cluster-model has been ascertained.

The work presented in this thesis can easily be expanded upon. There is still much work to be done to understand the molecular mechanisms resulting in film growth for both TMA/H₂O and DEZ/H₂O processes. Modelling the growth of an amorphous alumina is a huge obstacle. With some additional DFT calculations, the reaction mechanisms of publication I could be incorporated in a kinetic Monte Carlo model for Al₂O₃ growth. Modelling the amorphous growth of Al₂O₃ is beyond the on-lattice kMC model, but it would be interesting to compare the growth of different crystalline lattices of α- and γ-Al₂O₃ with respect to experimental growth rates using kMC.

The ZnO growth needs to be further investigated. As discussed previously, the set of reaction mechanisms for the DEZ/H₂O is missing a mechanism for surface ligand elimination. It is likely that the mechanism requires a surface environment more complex than has previously been studied, such as a step or kink on the surface. The mechanism may well be proton transfer reaction or a some kind of pyrolysis mechanism, where the ethyl-ligands react with each other to form butane or ethene.

In addition this, the surface chemistry at other lattice orientations should also be investigated. At low and high temperatures, the dominant lattice orientation is not (100) but the polar (001) surface. Due to the polar nature of the surface, it is difficult to model computationally.

An interesting new field within ALD is the deposition of organic–inorganic hybrid thin films. While *ab initio* modelling has been used to simulate particular parts of an MLD process in the past, the computational modelling of the growth process has not yet been investigated. The simu-
Results and Discussion

The simulation of an ALD/MLD process is demanding as it requires a large simulation cells, inclusion of weak interactions relevant in the case of organic molecules and a detailed description of the substrate surface before the organic reactant pulse. The simulations presented in this work, especially the saturated structures after the metal precursor pulse, serve as an excellent starting point for investigating the kinetics of an organic precursor during MLD.

As a novel approach, one might try to assess the reactivity of a precursor a priori using the chemical reactivity theory. This would allow probing several precursors before conducting a large scale DFT simulations. As an example, the reactivity of a set of precursors (diethylzinc, dimethylzinc, trimethylaluminium, triethylaluminium and aluminium trichloride) can be mapped on the global electrophilicity index of the precursor. The electrophilicity $\omega$ in chemical reactivity theory is defined as

$$\omega = \frac{\mu^2}{2\eta}$$

(4.2)

where $\mu$ is the chemical potential $\mu = \left(\frac{\partial E}{\partial n}\right)_v$ and $\eta$ is the chemical hardness defined as

$$\eta = \left(\frac{\partial^2 E}{\partial n^2}\right)_v.$$  

Electrophiles accept electrons and, hence, molecules with large electrophilicity are Lewis-acids. The metal precursors in ALD are Lewis-acids and there is promising correlation between the electrophility of a precursor and its reactivity. In figure 4.10 the global electrophility of the precursors mentioned above is compared with the activation energy of the removal of the first ligand on ZnO and Al$_2$O$_3$ surfaces.

The correlation between the global molecular descriptor (electrophilicity) and the initial reactivity of the precursor suggest that molecular properties could be used to predict the reactivity of a precursor as a prescreening procedure. It would be interesting to see if the experimental growth rates of a set of precursors at fixed temperature and pressure could be statistically correlated with, say, the electrophilicity of a precursor and, say, the size of the precursor ligand.

However, it may not be obvious which precursor forms the bottle-neck for the overall process. The removal of the first ligand may have a low activation energy, but the barrier may be high for other ligands. For example, in the case of zinc oxide we observe while the DEZ is very reactive
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Figure 4.10. Activation energies for a set of molecules on ZnO and Al₂O₃ surfaces. The global electrophilicity obtained from eqn 4.2 correlates with the initial reaction barrier of the molecules.

at the surface, the monoethylzinc is quite inert and the water pulse kinetics limit the growth of the thin film.
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5. Conclusions

To understand an atomic layer deposition process, the chemical mechanisms that convert the precursors into the thin film need to be understood. This mechanistic picture can be difficult to ascertain from experiments and density functional theory calculations are a useful tool for investigating the relevant chemical processes on the substrate surface. DFT can be used to understand the atomic level phenomena responsible for the deposition of a thin film during ALD by studying the thermodynamics and kinetics of the surface reactions and to estimate surface saturation structures.

The focus of this thesis is the key reaction steps contributing to growth of Al₂O₃ and ZnO thin films via atomic layer deposition. Quantum mechanical modelling of atomic layer deposition allows for an atomistic perspective of the growth process that often reaches beyond experimental methods. Theoretical calculations help to interpret experimental data and provide valuable insight to the process. The mechanistic insight obtained from the quantum mechanical calculations is used to construct a kinetic model of the ALD of ZnO, allowing a direct comparison with experimental data.

Our study on the TMA/H₂O process (publication I) expands on previous investigations by using a hydroxylated Al₂O₃ surface model. The hydroxylated surface is a more realistic description of the α-Al₂O₃ (0001) surface at the process conditions than the gibbsite model used in previous studies. There is a clear difference in the surface reaction energetics between the two surface models, so the chosen substrate model for the simulations has a large effect on quantitative results obtained from the simulations.

Our calculations show that trimethylaluminium is very reactive on both
bare and fully hydroxylated Al₂O₃ surfaces and rapidly fragments to dimethylaluminium and further to monomethylaluminium as methyl-ligands are eliminated by the surface hydroxyl groups. The formation of methyl-bridges was observed between surface groups that stabilized adsorption of TMA through cooperative effect. The relative reactivity of these surface fragments suggests that at saturation the surface will mainly consist of dimethyl- and monomethylaluminium species.

The surface kinetics for the subsequent water pulse were found to be accessible at process conditions. The elimination of MMA on the surface by an isolated water molecule was estimated to be inaccessible but cooperative effect between two or three water molecules was observed to stabilize the transition state, leading to a lower activation energy.

The rest of the thesis focuses on the DEZ/H₂O process by investigating the surface mechanisms for each reactant pulse (publications II-III) and by constructing a kinetic model for the overall deposition process (publication IV). These studies focus on the homodeposition of ZnO in the (100) lattice orientation. This surface is predicted to be fully hydroxylated, with the water molecules forming a periodic 2×1 structure of alternating associated and dissociated water molecules.

Diethylzinc was found to be very reactive; adsorption of DEZ onto the hydroxylated surface is exothermic and a reaction with a surface hydroxyl group has a low barrier. However, the subsequent reactions for monoethylzinc with surface hydroxyl groups were found to have a high activation energy, rendering the monoethylzinc inert. In addition to calculations on the planar (100) surface, DEZ reactions on two hydroxylated surface steps were investigated. The barrier for the reaction between surface hydroxyl groups and DEZ increased in both cases. However, for one of the step structures a lower barrier for elimination of the monoethylzinc was found.

The lowest activation energies obtained suggested that ethyl-ligands were eliminated in two distinct steps: removal of the ligand from DEZ with a low barrier on the order of 0.5 eV and from MEZ with a moderately high barrier of 0.95 eV. Based on this, two estimations for the ethyl-saturated ZnO surface were created for a low and high temperature deposition ranges. These saturated structures were found to be in good agreement with experimental data.
The water pulse reaction steps were studied on the ethyl-saturated surface structures as well as on an isolated monoethylzinc site. Overall, the barrier for eliminating the surface ethyl-ligands were high, in most instances above 1 eV. This suggests that the water pulse reaction kinetics are the limiting factor in the ALD cycle, a result confirmed by experimental data. As in the case of Al2O3 deposition, water–water interactions were found to stabilize the transition states through cooperative effect. Cooperative effect was observed also in the adsorption of water; the presence of several monoethylzinc on the surface lead to strong adsorption bonds for water.

The mechanisms for both DEZ and water pulses were implemented to a kinetic Monte Carlo code in collaboration with Dr. Mahdi Shirazi and Dr. Simon D. Elliott. The kinetic model correctly reproduces the temperature dependence of the thin film growth rate and is in good quantitative agreement with experimental measurements. The onset of the film growth is correctly predicted by the model. The kinetic model confirms our interpretation of the overall process: the incomplete elimination of the ethyl-ligands results in low growth per cycle at low temperatures. At elevated temperatures, the elimination of ethyl becomes accessible and the average growth per cycle increases rapidly, reaching a maximum at the "ALD window".

In summary, the work conducted in this thesis shows that the surface processes contributing to the deposition of oxides are complex, involving several cooperative processes. Computational quantum mechanics provides valuable insight and is a powerful tool for modelling the molecular chemistry of ALD. An explicit surface model is required if one is to capture the mechanisms relevant to the overall process. Kinetic Monte Carlo is a suitable tool for modelling the growth of the film as the complex cooperative effects can be implemented into the reaction network.
Conclusions


References


References


References


References


Thin films form the foundation of microelectronics and are a fundamental aspect of modern technology overall. Atomic layer deposition is an important thin film growth technique, developed in Finland in the 1970s, that allows the deposition of films at atomic resolution.

Computational quantum chemistry is a powerful tool for studying atomic level phenomena such as molecular adsorption and chemical reactions. Density functional theory is computationally efficient approach for modelling periodic systems consisting of hundreds of atoms.

The fundamental understanding of atomic layer deposition lies on the mechanistic interpretation of the surface processes leading to film growth. In this work, atomic layer deposition of aluminium and zinc oxides was studied using density functional theory. The key reaction steps are identified and from the kinetics of these surface reactions, the evolution of the overall process can be understood.