Modelling of nanoscale phenomenon : quantum dot nucleation

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MODELLING OF NANOSCALE PHENOMENON - QUANTUM DOT NUCLEATION

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ABSTRACT

There has been a tremendous increase in interest on gallium nitride (GaN) since 1989 when it was shown by the Nichia group [1], the possible capabilities obtainable from GaN. However it was only recently that intense research efforts have been dedicated to developing high-quality GaN due to the recent breakthroughs in epitaxy techniques to grow GaN [2,3]. High quality GaN is difficult to grow due to its high susceptibility to form dislocations [4], need of extreme conditions for growth and the lack of lattice-matched substrates [5,6]. With recent available epitaxy techniques, some attention had been given to growing GaN quantum dots. Quantum dots (QDs) are nano-islands or structures that exhibit zero-dimension density-of-states and are ideal for use in various optical and opto-electronic applications [7]. However, due to their extreme small size, precise instrumentation for *in situ* monitoring of their growth process is not available. In addition, GaN QDs have in many ways displayed unique growth characteristics, which are different from other group III-V quantum dots systems such InAs/GaAs. Hence, it is proposed here to conduct an atomistic simulation to study the nucleation process of GaN QDs on aluminium nitride (AlN) substrate.

There are various types of atomistic simulation techniques and these can be classified into 3 categories: Molecular Dynamics (MD), Monte Carlo (MC) and Hybrid Monte Carlo (HMC). From a literature search on GaN growth using atomistic simulations, it was noted that there are very few using MC techniques and the reason can be attributed to the lack of pre-defined properties required for the MC method. Hence, the techniques available for vapour deposition application are limited to MD or HMC.

Similar in both techniques, a potential function is required to describe the interatomic/intermolecular behaviour in the simulations. Currently, there are eight different potential functions that have been fitted to describe the properties of GaN. A study of the potential functions was made and a list of selection criterion set up to select the most suitable potential for the simulation. The Stillinger-Weber (SW) potential was eventually chosen. However, before the SW potential can be applied to the model, it

required a test to check for its range of thermal stability, which has not been carried out before. A simple heating was first conducted and the thermal stability range was found to be ~ 1950 K. A melting simulation was next conducted and the melting temperature displayed by SW potential was around 2050 K. From these tests, it was concluded that the SW potential is thermally stable for the vapour deposition simulation at 1023 K ($=750^\circ\text{C}$).

Next, as MD is extremely compute intensive and the problem cannot be simplified due to the 3-dimensional QD structure, a series of preliminary tests – deposition test and impact test – were designed and conducted to gauge the level of compute resources required. From the two tests, it was found that at least 10 unconstrained atomic layers are necessary to simulate a bulk substrate behaviour. Considering the computation costs, HMC method was chosen for use in the vapour deposition simulation of QD nucleation.

Since the objective of the simulation was to observe the nucleation of the adatoms, the substrate atoms were taken to be fixed. To further reduce the computational cost, the simulations were initiated on the wetting layer. The vapour deposition simulation was conducted for a series of different Ga/N ratio of 1.0 (stoichiometric) and 2.33 on Ga-terminating and N-terminating surfaces of commensurate and strain-varied (unrelaxed) GaN wetting layer. The simulation results show the rough growth obtained for Ga/N ratio $= 1.0$ on N-terminating (unstrained) surface and a smoother growth for Ga/N ratio $= 2.33$ on N-terminating surface and Ga/N ratio $= 1.0$ on Ga-terminating surface. As for the strain-varied surfaces, the QDs were observed to prefer nucleation locations with the minimum lattice distortions in the surface.

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CHAPTER 1

INTRODUCTION

1.1 Background

Since the first demonstration of the capability of the blue light laser by the Nichia group in 1989, gallium nitride (GaN) has since received immense interest to both scientists and industrial researchers [1]. The importance of the blue light LEDs (light-emitting diodes) is that it can achieve higher speed and higher density optical memory in compact disk applications. In addition, it has higher chemical and thermal stability than Si. For the past few years, significant levels of funding have been dedicated to the development of GaN growth techniques and it is foreseen that a realization will be fulfilled within the next 4 years [2, 3].

However GaN is not an easy material to grow and achieve with high quality compared with Si. In fact, it is extremely difficult to grow high quality bulk GaN crystal with low dislocation density from melt and epitaxy process, the two common techniques for growing bulk crystal. There are a few reasons for this difficulty, namely due to the lack of a lattice-matched substrate causing various dislocations to form, and the requirement of extreme conditions (150k atm nitrogen pressure and 1600°C – conditions reported used by TopGaN [4] during growth.

In addition, GaN is highly susceptible to dislocation formation due to its polytypism characteristics, i.e. it can exist in either zincblende, wurtzite or rocksalt structures, with the wurtzite structure being acknowledged to be the most thermally stable. Due to the similarity of the energy of formation of either of the structures (zincblende and wurtzite), various deformations, such as point dislocation (zero dimension), thread dislocation (one-dimension), areal dislocation (area dislocation, usually known as stacking faults) form easily during the growth process, especially when a lattice-mismatched substrate is used [5]. Another problem is that most of the typical substrates – SiC, Al₂O₃(sapphire), etc (used for growing GaN thin film has a relatively smaller thermal expansion coefficient compared to GaN, causing cracking during the cooling process [6].

Henceforth, there was little progress in the understanding of GaN until recently, when there was a breakthrough in the epitaxy technique to grow GaN thin films [1]. With this new breakthrough, some of the research focus has been turned towards growing other nanostructures such as GaN quantum dots.

Quantum dots (QDs), hereby defined as semiconductor nanostructures or islands grown on a semiconductor substrate, were first reported by Goldstein *et al.* in 1985[7] and has since been an area of intense research interest due to their electronic and opto-electric properties. From the literature, there are many different systems of QDs, namely different QD materials on different substrates. Most QD systems are grown via the Stranski-Krastanov (SK) mode, in which a transition from 2D (thin film) to 3D (QD) is observed. Although various QDs are achieved from the same SK mode, the different QD and substrate materials combination will result in a great variety of properties and growth characteristics. One such example is the GaN/AlN (GaN QDs on aluminum nitride, AlN, substrate). GaN/AlN QDs have been observed to display very different growth characteristics and may possibly involve other properties (such as their polarity and polytypism characteristic), which are very different from Si/Ge and InAs/GaAs, the two best-researched QDs system in literature.

Due to the extremely small size of the QD and the lack of *in situ* monitoring during growth, very little is known about their formation, except that the growth is usually highly diffusion-biased by strain variation on the growing surface. Various theorems have been developed to describe their formation in terms of surface energies and the deposition process. However, these theorems seem to work for some QD cases but fail for others. In addition, these theorems are usually based on continuum approaches which may be unsuitable as QD sizes range from a few hundred to at most a few thousand atoms. Hence, atomistic simulation has been acknowledged as the alternative to understanding the QD formation process and will be used in this project to investigate the vapor deposition and GaN QD nucleation process.

Chapter 1: Introduction

1.2 Objectives

The objectives of this project are as follow:

- To study the current atomistic techniques for vapor deposition simulation
- To develop a model to simulate the GaN/AlN QD nucleation process via strain-driven diffusion

1.3 Layout of report

In chapter 1, a brief overall introduction on the existing problems of GaN and QDs is presented with a view to the reasons of using atomistic simulation methods to investigate the nucleation process of GaN QDs.

In chapter 2, a literature review is made on studies conducted on the material properties of GaN, epitaxy growth techniques used for QD growth and the general research that have been done on QDs with an emphasis placed on GaN/AlN QDs.

In chapter 3, a study of the different simulation techniques and simulation work done carried out on GaN in literature is presented. From the research, GaN has been intensively studied by MD methods and hence MD or hybrid Monte Carlo (HMC) methods are proposed for use in this project. Both simulation methods required the usage of a potential function and Stillinger-Weber (SW) potential is selected. However, it is found that the thermal stability at the simulation temperature has not been tested.

In chapter 4, some of the basic elements of MD applied is introduced. Testing of the thermal stability of the SW potential is performed via heating. Subsequently, a melting simulation is conducted.

In chapter 5, two tests – deposition test and impact test – are designed and carried out to gauge the possible required computational power. The determination of the computational power is critical in deciding the type of simulation (MD or HMC) to be applied for the vapor deposition simulation. From the two tests, it has been found that MD is too computationally intensive and hence HMC is opted for use. Since HMC

is highly dependent on the random number generated, a test on the ‘randomness’ of the different random number generators – *ran()* and *ranf()* is performed.

In chapter 6, the overview of the HMC simulation design and procedure is provided. Vapor deposition simulation is carried out on a commensurate GaN wetting layer strained to the lattice of AlN. The conditions tested are: Ga/N ratio = 1.0 and 2.33, for Ga-terminating and N-terminating surfaces of Ga-polarity GaN. Tests results on vapor deposition on an unrelaxed strained-varied substrate under Ga/N ratio = 1.0 are then presented.

In chapter 7, observations from the simulations are discussed and compared to experimental data reported in literature. The possible errors in the results and suggested methods to overcome these errors are then ensued. Possible future work is also proposed.

In chapter 8, a conclusion is made on the work performed and the objectives achieved.

CHAPTER 2

LITERATURE REVIEW

2.1 Gallium Nitride

It is important to study properties of GaN in order to understand its problems related to its tendency to form high dislocation densities and its main characteristic, namely its polarity due to the wurtzite structure. It is believed that its polytypism and polarity may provide an insight to its QD formation and thus useful inputs into the modelling process.

GaN has a high bandgap energy of 3.4 eV, the required bandgap energy for blue LEDs. In addition, GaN has other desirable properties such as:

- high chemical and thermal stability (compared to Silicon)
- high thermal conductivity ($1.3 \text{ W cm}^{-1} \text{ }^{\circ}\text{C}^{-1}$)
- high melting temperature (stable up to 1273 K in vacuum)
- low dielectric constant ($0 \sim 5.5$)
- high breakdown voltage ($\sim 5 \times 10^6 \text{ Vcm}^{-1}$ at 300 K)

suitable for application in optical, optoelectronic and electronic devices [8,9].

However, GaN possesses polytypism characteristics, i.e. it can exist in either zincblende or wurtzite structures under the same condition due to the similarity of the energy of formation of either of the structures as reported by Yeh *et al.* [5]. Consequently, various deformations, such as point dislocation (zero dimension), thread dislocation (one-dimension), areal dislocation (area dislocation, usually known as stacking faults) form easily during the growth process (both melt or epitaxial growth). Although several groups, such as the Cambridge centre for gallium nitride, have declared that the displayed properties of GaN remain good despite its high dislocation density ($10^{11}/\text{cm}^2$) [10], it is undeniable that with higher quality of GaN better performance can be obtained [4].

Currently, there is no commercialized GaN substrate of high quality or low dislocation density available in the world. This is because good quality GaN is difficult to grow from melt (Czochralski or Bridgman growth methods) and epitaxial process

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due to the lack of lattice-matched substrates with similar thermal expansion coefficient as GaN [6]. As reported by Karpinski *et al.* [4], high quality GaN can only be achieved with controlled processes via extreme conditions of high temperature (1600 °C) and high nitrogen pressure (150k atm). It was only until the recent advance of epitaxial technologies that GaN becomes once more the focus of intense research.

2.1.1 Crystal Structure

GaN can co-exist in the wurtzite or zincblende structures (as shown below) with the wurtzite structure being more thermodynamically stable [11]. In **fig2.1a**, a lattice unit of the wurtzite structure is shown. The wurtzite structure consists of two interpenetrating hexagonal close-packed (hcp) lattices offset by $[0\ 0\ 0\ \frac{3}{8}]$ from each other.

Fig 2.1a: Wurtzite structure

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A lattice unit of the GaN zincblende structure is shown in **fig 2.1b**. The zincblende structure is made up of two interpenetrating face-cubic centre (fcc) lattices offset by (0.25, 0.25, 0.25) from each other.

Fig 2.1b: Zincblende structure

Lattice Constants of Wurtzite polytype : $a = 3.189 \text{ \AA}$ and $c = 5.185 \text{ \AA}$

Lattice Constants of Zincblende polytype : $a = 4.25 \text{ \AA}$

(Values taken from ref. [12])

2.1.2 Polarity of GaN

The III-nitrides GaN, AlN and InN are essentially ionic solids with strong charge transfer between the more electronegative nitrogen atoms and the less electronegative metal atoms. This results in the III-nitrides wurtzite structure having a polar axis parallel to the c -direction (or $[0001]$) of the crystal lattice.

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Fig 2.1c: Ga-face polarity

Fig 2.1d: N-face polarity

In other words, the *c*-plane of the wurtzite GaN crystal is polar:

Chapter 2: Literature Review

Fig 2.1e: *c*-plane of GaN

Depending on the inclusion of the *c*-direction, other planes of GaN can be non-polar or semi-polar [13]. Some of the most common planes of GaN are shown:

Fig 2.1f: *a*-plane (left), *r*-plane (centre), *m*-plane (right)

This polarization is absent in the zincblende structure due to its higher lattice symmetry as commented by Potin *et al.* [14].

There are various groups which have tried different approaches in determining the polarities of GaN by AES (Auger electron spectroscopy), CBED (convergent beam electron diffraction), Rutherford backscattering ion channelling technique and chemical etching. However, their testing tend to investigate only the superficial surface of the GaN rather than the structure itself. These tests are based on the assumptions that the Ga-face polarity will have a Ga-terminating surface and the N-face polarity will have a N-terminating surface, due to thermodynamic stability. From the available experimental work, Hellman [15] proposed a set of guidelines as a standard framework:

1. The smooth side of an un-doped, as-grown GaN plate-like bulk crystal is N-face and the rough side is Ga-face.

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2. Ga-face GaN grows on Si-face SiC and N-face GaN grows on C-face SiC
3. Films with hexagonal pyramidal morphology grown on sapphire are N-face. Smooth films grown by MOCVD are usually Ga-face.
4. The Ga-face of GaN is chemically more stable than the N-face. KOH and NaOH solutions will etch the N-face but not the Ga-face. The N-face will decompose rapidly at 900 °C in hydrogen.
5. The relationship of the piezoelectric and crystallographic axes in GaN is like that in ZnO, so that the Ga face $\text{Al}_x\text{Ga}_{1-x}\text{N}$ -on-GaN interface has an enhanced 2-dimensional electron density.
6. The clean GaN N-face can be identified by a series of surface constructions between 100 °C and 300 °C which include a (3×3) reconstruction. (2×2) reconstructions are frequently observed on the clean Ga-face.

These sets of guidelines are derived from the observed characteristics of the polar faces of GaN and cannot be taken as conclusive as there may be deviations (e.g. N-terminating surface at Ga-face and Ga-terminating surface at N-face) which will result in conflicting conclusion of the true polarity.

However, the difficulties of controlling and determining the polarity of GaN does not end here. In GaN, both polarities can coexist side by side on the same substrate, resulting in inversion domain boundaries (IBD) thus complicating the investigation.

The polarity is also found to affect the growth rate of GaN. Liliental-Weber *et al.* [16] were among the first to report the importance of the polarity in the growth. They tested the growth rates at different crystallographic directions of GaN and had found that the growth in the non-polar direction $[1\ 1\ \bar{2}\ 0]$ to be the fastest – 50~100 times faster than the Ga-face polarity $[0\ 0\ 0\ 1]$. In fact the growth rate in the Ga-face polarity was reported to be 2~2.5 times faster than that of the N-face polarity [6]. A reason had been proposed by Liliental-Weber *et al.* [16] for this observation in the differences of growth rates between the Ga-polarity and that of the N-polarity was due to the much lower absorption rate of the N adatom compared to the Ga adatom.

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2.1.3 Dislocations – Stacking Faults

Other than the different growth rates at different polarities, different types of defects are found to form preferentially in layers grown under different conditions [6]. Threading dislocations and a low density of $5 \times 10^2 \text{ cm}^{-2}$ of IDB, originating at the substrate interface, are found to be more common in epilayers grown in the Ga-polarity. On the other hand, good epilayer/substrate interface is achieved on the N-polarity but with typical defects of extrinsic dislocation loops along the c-plane and pinholes in the epilayer.

The main reason that GaN thin films suffer from many types of dislocations is due to generalized (structural, thermal) mismatch between the GaN epilayers and the substrate. It was only until recently that the technology to grow bulk crystal GaN substrate of high quality has matured [4], though it has not been commercialized yet. The typical substrates used to grow GaN are sapphire (Al_2O_3), SiC, ZnO, LiGaO_2 , MgAl_2O_4 , MgO, Si (for cubic), GaAs (for cubic).

GaN-based devices are known to be sensitive to long-extended dislocations but the extent to which these dislocations affect the performance in terms of the quantum efficiencies and the device lifetimes are still unknown [10,17]. In fact, commercialized blue GaN LEDs, which have dislocation densities as high as 10^9 cm^{-2} , are known to give sufficiently good performance. This relatively good performance of GaN LEDs were puzzling until *ab initio* results revealed that among the dislocations, certain dislocations such as charge-neutral edge and screw threading dislocations are electrically inactive and therefore do not contribute to the energy bandgap states [18]. However, other types of dislocation such as edge dislocation have been studied using *ab initio* methods and may or may not be electrically-active, resulting in deep-gap states in the electronic devices.

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Some of the long-extended dislocations of GaN are as follows:

Threading edge dislocation

Fig 2.1g: Threading edge dislocation (taken from Ref. [21])

Threading edge dislocation has been studied by Blumenau *et al.* [18] by calculating the energies involved using *ab initio* techniques. From their analyses, they had opposed the results by Wright *et al.* [20,21] and concluded that threading edge dislocation to be electrically-inactive unless an active donor atom, usually Oxygen, is involved. However, they also proposed that electrically active donor and acceptor pairs can be trapped at the core of the threading edge dislocation and in the dislocation stress field, thereby resulting in a negatively-charge dislocation responsible for the yellow luminescence in GaN.

It should be noted that the yellow luminescence mentioned corresponds a lower energy level compared to the blue (higher energy level) for GaN in PL (photoluminescence), which is a surface technique for probing the energy levels in a sample.

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Inverse domain boundaries

Fig 2.1h: Inversion domain boundaries (IDB)

Stutzmann *et al.* [11] investigated the electronic and structural properties of both polarities as well as mixed polarity [11]. From their experimental analysis of Ga-, N- and mixed polarity, they concluded that the polarity of the GaN is controlled by the thickness of the AlN nucleation layer. The electron mobilities for the Ga-face and N-face polarity are found to be similar ($1000\sim 1200\text{ cm}^2/\text{Vs}$) but a much lower electron mobility is obtained for that of mixed polarity ($0\sim 500\text{ cm}^2/\text{Vs}$). A more reliable way of determining the polarity was suggested whereby the examination of the crystal structure and atomic positions to be carried out via X-ray diffraction (XRD) and other similar microscopic techniques.

Stacking faults

There are 3 types of intrinsic stacking faults and 1 type of extrinsic stacking fault. The intrinsic stacking faults are classified as Type I, Type II and Type III, according to the number of violations of fault layers. A detailed description of each stacking fault is as follows:

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- Type I Stacking Fault:

Fig 2.1i: Type I Stacking fault

In the type I or I_1 stacking fault, there is one violation in the stacking rule. There are 2 possibilities in this stacking fault – it can occur at the Aa layer (AaBbAaCcAaCcAa...) or the Bb layer (AaBbAaBbCcBbCc...). The capital letters in the sequence represent the layer of Ga atoms and the lowercase letters the layer of N atoms. This fault can be formed by the removal of a basal layer followed by a shear of $1/3$ $(1\ 0\ -1\ 0)$ of the wurtzite crystal. The stacking fault formation energies per unit area is the lowest among the stacking faults as reported by Liliental-Weber *et al.* [6] and is estimated by Stampfl *et al.* [17] to be around 10 meV.

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- Type II Stacking Fault:

Fig 2.1j: Type II Stacking fault

In the type II or I_2 , there are two violations in the stacking rule and is estimated to have the highest energy among the intrinsic stacking faults. This fault can take the sequence of AaBbAaBbCcAaCcAa... as shown in **fig 2.1h**. It can a result from a shear $1/3 (1\ 0\ -1\ 0)$ in an originally perfect wurtzite structure. The formation energies per unit area is estimated by Stampfl *et al.* [17] to be 24 meV.

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- Type III Stacking fault:

Fig 2.1k: Type III Stacking fault

In type III or I_3 , one of the Aa or Bb layer is replaced by a Cc layer, thus resulting in a violation of stacking rule. It can be of the sequence BbAaBbAaCcAaBbAa... or AaBbAaBbCcBbAaBbAa... It is estimated by Stampfl *et al.* [17] to have the second lowest formation energy per unit area of 19 meV.

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- Extrinsic Stacking Fault:

Fig 2.11: Extrinsic Stacking Fault

In the extrinsic or type E stacking fault, an additional Cc layer is inserted into a normal stacking sequence. An example of this sequence is AaBbAaBbCcAaBb... This type of fault is estimated by Stampfl *et al.* [17] to have the highest formation energy of 38 meV per unit among all the stacking faults.

These stacking faults arise during growth due to the lack of a lattice-matched substrate. These stacking faults are found by *ab initio* calculation to be electrically-inactive, i.e. they do not induce any states in the band gap energy. However, this fault can result in quantum-well-like region of zincblende material within the wurtzite structure and can cause the binding of electrons [14,17]. One of the main problems of stacking faults is that it is difficult to detect via non-destructive methods such as Burger circuit. It has been shown by Potin *et al.* [14] that Burger circuit drawn around stacking faults does not show any closure failure. Generally, stacking faults are observed using microscopic techniques such as HREM (high resolution transmission electron microscopy).

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2.2 Epitaxial Growth Techniques

QDs are typically grown epitaxially by MBE or MOCVD. The growth mechanism and conditions are widely different in these two techniques. Hence in order to model the simulation process realistically, an understanding of these two epitaxy methods is first needed before selection of a suitable technique to model.

2.2.1 Molecular Beam Epitaxy (MBE)

Molecular Beam Epitaxy (MBE) transports the growing species in the form of the beam during the deposition process and hence its name. There are 2 types of transport system:

- Physical transport techniques or physical deposition techniques (PDT) in which the growth species are vaporized at high local temperature and are transported towards the substrate in the form of thermal-energy beam without any chemical change
- Chemical transport techniques or chemical deposition technique (CDT) in which the volatile species containing the constituent elements of the growth material are transported towards the substrate in the form of a beam. Subsequently, these species undergo chemical reactions to form the necessary growth species.

Fig 2.2a: Deposition of MBE (taken from ref. [22])

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In MBE, ultra high vacuum (UHV – Pressure $<10^{-9}$ Torr) is used. This is necessary to ensure that there is no interference during the transport of the growth species to the substrate surface. To ensure this UHV within the deposition chamber, the walls of the chamber is surrounded by a cryopanel or cryogenic shroud, containing liquid nitrogen, providing additional pumping of residual gas. Other functions of the cryopanel are to prevent re-evaporation from parts other than the hot cells and provide thermal isolation among the different cells.

Typically, the following standard equipment are incorporated into the deposition chamber [22,23].

Effusion cell

The effusion cell is used for containing and heating the substance used for the deposition process and as a means to transport material from the outside into the deposition chamber. Each effusion cell is equipped with a shutter which is used to interrupt the beam and block further deposition of the material from the cell. The effusion cell is designed for an operating temperature of up to 1400 °C and has to be made of materials which are stable at this temperature. Also, the material used should not outgas easily within this temperature range (some materials will give out gases at high temperature and thus will add impurity into the MBE system). A typical material used is for the crucible in the effusion cell is the PBN.

Cracker cell

The cracker cell is similar to the effusion cell with an additional cracker furnace which function is to ‘crack’ the gaseous molecules into smaller molecules or atoms (e.g. As₄ to As₂). Typical materials used for the cracking furnace are graphite, tantalum, molybdenum and PBN.

RHEED

A RHEED (refraction high energy electron diffraction) gun is incorporated to allow for in-situ detection of the deposition process. A fluorescent screen is placed opposite to the RHEED gun so as to show the diffraction of the electron beam from the substrate.

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Mass Spectrometer

A mass spectrometer is required for measuring the mass of the gaseous atom so as to detect the gaseous elements present in the deposition chamber

Flux (ionization) gauge

The effusion cell temperature used determines the amount of flux and hence pressure of the gas particles during deposition. The flux gauge is used for measuring the pressure of the gas or beam so that the cell temperature can be tuned to the required amount of flux prior to the deposition process.

Substrate-holder

The substrate-holder or manipulator is used to hold the substrate in place and in the directions of the beams during the deposition process. A heater is also included here so as to heat the substrate and maintain the temperature throughout the growth process. In addition, the substrate holder is designed with a CAR (continuous azimuthal rotation) assembly so as to rotate the substrate to ensure uniform exposure of the beams throughout the surface of the substrate. Similar to the effusion cell, a shutter is also incorporate to the substrate-holder to prevent further deposition on the substrate.

Fig 2.2b: Three zones in MBE

Fig 2.2b shows a simplified diagram of the deposition process. There are 3 zones in the MBE deposition process – generation zone, mixing zone and crystallization zone. The generation zone consists of the effusion cells that are responsible for generating the atomic beams required for deposition. The beam flux must be tilted so that it converges at the substrate and covers the whole cross-section. The mixing zone

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is the zone whereby all the atomic beam fluxes intercept. It must be noted that even if the atoms collide with one another, no reaction may occur due to the lack of a base for reaction. In the crystallization zone, the atoms from beam flux may react with one another and the substrate atoms to form a crystalline film.

Fig 2.2c: Deposition process in MBE

At the crystallization zone, a series of surface processes can occur:

- Absorption of atoms or molecules impinging on the substrate surface
- Surface diffusion of the absorbed atoms or molecules along the surface of the substrate
- Chemical reaction of the absorbed atoms or molecules with the substrate atoms or the epilayer already grown
- Thermal desorption of the unreacted atoms or molecules.

The surface process can be described by the thermal accommodation coefficient, a , which describes the extent to which the arriving atoms reach thermal equilibrium with the substrate:

$$a = \frac{T_i - T_e}{T_i - T_s}$$

where, T_i is the effusion cell temperature

T_e is the evaporation temperature of the atom

T_s is the temperature at which thermodynamic equilibrium is achieved

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and the sticking or condensation coefficient, s , which is the ratio of the number of atoms adhering to the substrate surface to the number of atoms arriving there:

$$s = \frac{N_{adhere}}{N_{total}}$$

where, N_{adhere} is the actual number of atoms that stay at the substrate

N_{total} is the total number of atoms arriving at the substrate

It should be noted that the sticking coefficient plays a role of higher importance than the accommodation coefficient as it describes whether the atoms remain absorbed to the substrate. Different atoms or molecules will have different sticking coefficients. Hence, if several atom types are involved in the epilayer, their sticking coefficients have to be considered. For example, in GaN, the N atoms have a much smaller sticking coefficient than the Ga atom. Hence they will desorb more readily. To overcome this situation, the N/Ga ratio (the ratio of the number of N atoms to the Ga atoms in the beam flux) is generally > 1 and that the N pressure must be retained throughout the growth and cooling process as reported by Gogneau *et al.* [24].

There are two types of absorption processes:

- Physical absorption or *physisorption*, in which there is no electron transfer between the absorbed atom and the substrate atoms. The interactive forces involved can be attractive van der Waals forces and Coulombic interaction.
- *Chemisorption*, in which there is a chemical reaction occurring between the absorbed atom and the substrate atoms, resulting in a transfer of electrons and the forming of bonds. The bonds formed (covalent or ionic) depend on the types of atoms involved in the chemical reaction.

2.2.2 MOCVD

MOCVD stands for metalorganic chemical vapor deposition. An alternative name for MOCVD is MOVPE (metalorganic vapor phase epitaxy). As the names imply, metalorganic sources are used as its growth species.

The alky compounds used in the MO sources contain organic radicals that have one or two carbon atoms and are usually moderately volatile liquid at room

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temperature. These compounds will undergo pyrolysis or decomposition at high temperatures (500 °C – 800 °C). For example, the commonly used alkyl compound for Ga is TMGa (trimethylGallium) – $\text{Ga}(\text{CH}_3)_3$. For the Group V sources, hydrides of the Group V element are usually used – AsH_3 and PH_3 . Due to the need to produce the growth species, it is important to ensure that the growth temperature is sufficiently high for the pyrolysis of the sources to occur.

Fig 2.2d: Schematic of MOCVD

The MOCVD system consists of the following major parts:

Gas handling system

The gas handling system must be clean and leak-tight to prevent impurities from the outside environment from entering into the system. Carrier gases are used to carry the MO alkyls sources, hydrides and dopants into the reactor chamber. The typical carrier gases used are nitrogen and hydrogen. These carrier gases have to be purified to a purity of $\sim 10^{-10}$ level before they can be delivered to the system.

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Fig 2.2e: Source bubbler

The carrier gas is then bubbled through the source bubbler. A cooling bath, surrounding the source bubbler, with temperature controller is used to ensure the source bubbler is at a constant temperature. An electronic mass flow controller is used to control the flow of carrier gas as well as to maintain a constant vapour pressure of the source.

Reactor

The deposition process is conducted in the reactor. The growth species are carried by the carrier gas into this chamber. Consequently, the flow of the carrier gas must be ensured to be laminar so as to allow for control of the deposition process (deposition rate, temperature, uniformity of epilayer grown). Hence, reactors are typically designed to be

- Sufficiently long to allow the flow of the carrier gas to be fully developed (i.e. the flow across cross-section remains stable throughout the length of the tube) before reaching the substrate.
- streamlined (with very gradual change in diameter) so as to prevent any turbulent flow resulting from sudden change in cross-sectional area.

A heating system is incorporated into the for the pyrolysis of the sources. The typical heating method used are radio frequency (RF) induction heating, radiating (IR lamp) heating and resistance heating. The temperature is measured and controlled by thermocouples or pyrometers.

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In addition, to ensure the uniform spread of sources across the substrate, the substrate holder is designed to rotate the substrate throughout the deposition process.

Exhaust system

The exhaust system consists of the exhaust scrubber and other safety apparatus and is one of the most critical parts in the MOCVD in terms of safety. Most of the MO sources used are toxic, pyrophoric or easily flammable. Hence the exhaust system's main functions are to remove the un-reacted gases and by-products from the reactor and to provide a by-pass from the reactor. It is important to remove any blockages in the exhaust system as it may lead to a backflow of the gases and affect the uniformity of the epilayer growth.

Fig 2.2f: Liquid-based Scrubber

The scrubber is to reduce the concentration of the contaminants in vented gas to an environmentally-safe level so that the gases can be release safely into the environment.

The gases are first passed through a strong oxidizing agent, which is to precipitate the hydrides such as arsenic and phosphine into solid residues:

or

The existing gas from the acid solution is then passed through a strong alkaline to remove the bromide gas which might be released from the acid.

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2.2.3 Comparison between MBE and MOCVD

The advantages, disadvantages as well as similarities of the MBE and MOCVD are summarized in the following Table 1 and Table 2:

MBE	MOCVD
<ul style="list-style-type: none">• High flexibility, high growth rate achievable• Uniform, good surface finish, abrupt interface thin films can be grown	

Table 1: Similarities of MBE and MOCVD

MBE	MOCVD
<ul style="list-style-type: none">• relatively simple process and control• <i>In situ</i> monitoring is allowed• high shutdown time*• Require high purity level and ultra high vacuum within the system• Does not involve hazardous materials for growth	<ul style="list-style-type: none">• involves complicated chemical reactions and flow mechanisms for control• no monitoring of growth allowed• low shutdown time*• Require high level of purity but vacuum is not required• Used expensive reactants and hazardous MO sources

Table 2: Comparison between MBE and MOCVD

*: shutdown time is the time required for replacing a new substrate for growth. MBE requires high shutdown time due to the need to reduce the vacuum level. However, MBE allows the insertion of more than one substrate to reduce the shutdown time.

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2.3 Quantum Dots (QDs)

This section will be divided as follows:

- A brief introduction of the growth modes
- The experimental work done on QDs (focusing on the growth process)

2.3.1 Growth Modes

In the epilayer growth, there are 3 possible growth modes [25-27].

Fig 2.3a: Frank-van der Merve (FM) mode

In the Frank-van der Merve (FM) growth mode, the epilayers are grown layer by layer. This is the typical growth mode for thin films.

Fig 2.3b: Stranski-Krastanov (SK) mode

In the Stranski-Krastanov(SK) growth mode, a thin wetting layer of a few monolayers (depending on the substrate and growth material strain energy) is first formed until a critical thickness. Upon further deposition of the growth material, a 2D to 3D transition can be observed in which islands or clusters of the growth material of a particular shape (pyramidal or lens) form on the wetting layer. This growth mode is typical for semiconductors (e.g. Ge/Si, InAs/GaAs, GaN/AlN), in which a larger lattice material is strained as it is grown on a smaller lattice substrate.

Fig 2.3c: Volmer-Weber (VW) mode

In the Volmer-Weber(VW) growth mode, there is no wetting layer. Droplets of the growth material simply collect on the substrate. This growth mode can occur for semiconductors if the lattice mismatch is too high.

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There are 2 possible processes that are possible in the growth of QDs:

- Ripening process, in which a QD will grow in size at the expense of surrounding QDs (See Fig 2.3d)

Fig 2.3d: Ripening process

- Coalescence process, in which 2 or more QDs come together and form one single large QD (See Fig 2.3e)

Fig 2.3e: Coalescence process

2.3.2 Experimental Growth of QDs

QDs have been proposed and intended for various opto-electronic, optical devices. However, in all these QD application, there are 2 important requirements of the QDs, namely high density and uniformity in shape and size as commented by Xie *et al.* [28]. Up to date, there are in general 2 experimental approaches to grow QDs – using patterned substrates and by SK growth mode to achieve the above mentioned requirements.

In the first approach, patterns are made on the substrates:

- by electron-beam lithography and reactive ion etching [29-33]
- by masking via a shadow mask [34] or nanolithography [35,36]

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Fig 2.3f: Strained variations on patterned substrate

The basic concept of using patterned substrates is shown in **Fig 2.3f**. The nano-holes can be of various shapes (nanodimples, inverted pyramidal, cylindrical, etc). In the deposition process, the holes will collect the growth material prior to the formation of the wetting layer. As the growth material is filled inside the holes, it is allowed to be relaxed. Hence, when the holes are filled, strain variation is formed on the surface of growth with the strain being lower (or closer to that of the QD material) at the locations of the holes. Consequently, the wetting layer formed above the holes is thinner due to the lower strain at that position and the QDs are preferentially grown. Currently a high density of QDs around $10^9 \sim 10^{11} \text{ cm}^{-2}$ can be obtained by this method but it is important to note that this density is limited by the number of holes that can be made on the substrate.

The problems with this patterned substrates are: firstly, the crystal structure may be disturbed during the electron beam lithography and secondly, impurities from the chemical etching may remain in the holes [38].

Electron beam lithography process involves high energy electrons which will sputter as well as heat the substrate atoms in order to create the nanoholes. During the process, the substrate crystal structure where the electron beam hits may be seriously disturbed and may become amorphous. This creates a problem as the growth material may or may not be able to re-structure itself to retain the same crystal structure throughout. As a result, the electronic behaviour of the resulting devices may be affected.

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Impurities remaining from the etching chemical result in a similar problem. Due to the size of the nanoholes, cleaning is extremely difficult and impurities are unavoidable. The impurities may be electrically-active, i.e. become a donor or acceptor thus creating an unwanted band energy state in the device. In addition, the impurities may also cause dislocations to form within the growth material. Most electronic devices are very sensitive to impurities concentration as well as dislocation content. Hence, this approach may require further improvement before it can become a viable method to grow high-density and uniformly-sized QDs.

Alternatives method to patterned substrates is to form certain conditions that will allow the QDs to self-assemble preferentially at certain positions.

- steps naturally-formed on vicinal surfaces

Vicinal surfaces are surfaces that are a few degrees tilted away from a particular crystallographic direction (in this case, the growth plane) such that atomic steps are formed (See **fig 2.3g**).

Fig 2.3g: Vicinal surfaces

Due to the variation of the surface energy along the steps, QDs will form preferentially on the steps. The size of the QDs will also be restricted by the step-width and hence control over the size and density can be made by varying the step width and height.

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- By varying the strain pattern on the surface of growth (See Fig. 2.2h):

Fig 2.3h: Substrate morphology reported used in ref. [36]

In this approach, Schuh *et al.* [37] makes use of the strained pattern formed on an AlAs/GaAs superlattice laterally. Due to the variation of strain, the InAs QDs will form preferentially on region SL1 to SL4, which is an Al-rich region and on the surface above the AlAs layers. In addition, they reported that the size of the QDs grown corresponds to the thickness of the AlAs layer. This approach does prove to be a good way of controlling both the size and positions of the QDs. However, there are doubts if the final structure (superlattice and the QDs) can be applied in the design of the electronic devices and further investigation is required for this model.

So far, despite the numerous methods developed to control the growth of QDs in terms of its size and density, the SK growth mode is still the acknowledged best approach used for growing quantum dots.

Without any strain pattern or pre-patterning of the substrate, the growth conditions become the main issue for achieving high-density and uniform size QDs. The following are some of the growth conditions that will affect the growth of QDs:

- Substrate – crystal structure and the degree of lattice mismatch to growth material. In most cases, the substrate chosen has the same crystal structure as the growth material. The reason for this selection is the same as that for epilayer growth, which is to reduce the dislocation density in the grown material.

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It has been investigated and reported that lattice mismatch does affect the size of the QDs. In general, the substrate selected will have a $\sim > 2\%$ lattice mismatch as surmised by Chen *et al.*[42] (e.g. Ge/Si – 4%, InAs/GaAs – 7.2%) but this may differ for different QD/Substrate system. Another consideration that might be made is to ensure that the thermal expansion coefficients of the substrate and the growth material are close to prevent cracking during cooling.

- Surface of the substrate – Cleaning and processing of the substrate surface to remove any unwanted impurities before any deposition process is essential and can determine the quality of the epilayer grown. It is also important for the substrate to have a low dislocation density as some QDs may nucleate preferentially on these dislocations. In some cases, the dislocation may even be continued through the grown of the QD such as GaN/AlN QDs reported by Daudin *et al.* [39].
- Buffer layer, also known as *pseudo-substrate* – Buffer layer usually has 2 functions, namely to reduce the strain of the substrate and reduce the thermal expansion coefficient difference between the substrate and the growth material. The importance of the buffer layer can be seen from GaN/sapphire. In general, for the growth of all wurtzite GaN QDs, buffer layers (usually a series of AlN and GaN grown at a lower temperature) are required to reduce the strain as well as to prevent cracking during the cooling process [25,39-47].
- Temperature – of the growth material and that of the substrate. These temperatures may be different. In the growth of GaN/AlN QDs by MBE, the Ga effusion cell temperature is typically $< 921\text{ }^{\circ}\text{C}$ [44] and that of the substrate (sapphire or SiC with buffer layers) is around $700\sim 750\text{ }^{\circ}\text{C}$ [39,43,44]. In addition, the growth temperature is different for growing QDs and that for thin film of the same growth material on similar substrate [39,43]. For example in the growth of GaN/AlN QDs, Daudin *et al.*[39] had conducted similar experiments at different substrate temperatures and concluded that at relatively low temperature ($< 620^{\circ}\text{C}$), the relaxation of the GaN deposited on AlN is too small for QDs growth, hence resulting in FM growth mode for thin film.
- Growth pressure – Some QD growth material species may be more sensitive to growth pressure such as in the growth of GaN QDs on AlN. The nitrogen atoms in the QD will tend to desorb if the nitrogen pressure is not retained

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during growing and cooling process. Hence different pressures may have to be maintained during the growth process.

- Ratio of the growth species (applicable only for compound semiconductors) – Compound semiconductors require atoms from more than one element to form. However, the atoms of different elements have different behaviour and energies, resulting in different absorption rates. One example of such compound semiconductors is the III-V semiconductor, e.g. InAs, GaAs, GaN. In particular, GaN is found to be highly sensitive to this III/V ratio as N adatoms have a much lower absorption rates compared to the Ga adatoms.
- Coverage of the growth species – related to the deposition rate. It will affect the island density, size (aspect ratio) or even the growth mode. Typically, the islands will stop further growth in size and density after a certain amount of growth materials are deposited [24,41].
- Annealing time – after the growth of the QDs, the nanocrystal is allowed to anneal for a period of time. In general, the QD will increase in size by drawing additional material from the wetting layer until a certain stability is obtained. In some cases, annealing will cause Ostwald ripening, in which the island size will become very large and dislocations are formed within the QD [49].
- Growth interruption – The growth process is interrupted by stopping further deposition while retaining the temperature (the pressure may be varied). It is found that the QDs will evolve and become larger and more uniform in size and shape during this interruption [50,51]. However, it must be noted that the growth interruption conditions vary with different QDs system.
- Purity of the growth species – it has been known that dopants are impurities added intentionally into the growth material so as to create donor or acceptor atoms which can contribute to the properties of the various electronic and opto-electrical devices. Any impurities incorporated into the growth material may or may not be electrically-active and hence purity of the growth species will have to be very high to prevent unintentional doping. This is a major issue in epitaxial growth processes. In MOCVD, it is not possible to fully eliminate impurities as it requires the pyrolysis of precursors, which is a possible source of impurities, in order to obtain the growth material species. In MBE, ultra high vacuum ensures that no impurities from the outside enter the system and that

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materials used in MBE are carefully selected to prevent any out-gassing at high temperatures.

- Surfactants (or anti-surfactants) [52-55] – Surfactants are used to reduce the surface energy of the substrate and will increase the thickness of the wetting layer. (As and Sb as surfactants for Ge/Si; Te as surfactant for InAs/GaAs; Ga as anti-surfactant for GaN/AlN) In the case of gallium anti-surfactant in the GaN/AlN, excess gallium will prevent the growth of SK mode QDs and this layer of excess gallium will have to be desorbed before any 2D to 3D transition can be observed [41,44].

The controlling of the growth conditions differ slightly for the different epitaxy process used (MOCVD or MBE). In most growth process, a slight deviation in one or more parameters can result in a different observation of surface morphology. For example, in the growth of GaN/AlN, the typical Ga cell temperature used is around $< 921\text{ }^{\circ}\text{C}$. If this cell temperature is $1\text{ }^{\circ}\text{C}$ higher at $922\text{ }^{\circ}\text{C}$, Gogneau *et al.* [44] reported that the growth mode is FM and no QDs are observed. Tuning of each parameter, either independently or together with two or more other coupled parameters, is required before certain amount of control over the QDs grown is achieved.

Another control scheme of growing QDs is by growing stacked QDs. (see **Fig 2.3i**):

Fig 2.3i: Stacked QDs

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The idea to grow stacked QDs to obtain high-density, uniformly distributed and sized QDs was first proposed by Tersoff *et al.* in 1994 [56]. Basically, the growth process is similar to that of a single layer of QDs, except that a spacer layer was added after a layer of QDs was grown. After a certain thickness of the spacer layer, another layer of QDs is grown and the process is repeated. The spacer layer used may or may not be of the same material as that of the substrate and its thickness may be varied with increasing layer. The concept of stacked QDs is similar to that of the patterned substrate – to produce pronounced strain variation on the surface of growth, generated by the buried QDs below. Due to this strain variation, the deposited adatoms will have a diffusional bias and a preferential nucleation of the QDs at the local strain minima on the surface as analysed by Holy *et al.* [57].

It has been noted that there is an increase in size and spatial uniformity with increasing layers of QDs [56,58,59]. Due to the reduction of strain with increasing layers of QDs, the critical thickness of the wetting layer has been reported by Preister [60] to be reduced. In addition, there is a certain vertical and lateral correlation with increasing layers. However, the vertical correlation may not be always observed [56,61-63]. This means that the QD on the next layer may not nucleate directly above the lower buried QD, resulting in anti-correlation. There are many different proposed theories to this vertical correlation or anti-correlation.

There are many influencing factors for the vertical correlation of QDs and a summary was made by Springholz, 2005, as follows [64]:

Fig. 2.3j: Different mechanisms for the formation of interlayer correlations in QD superlattice (taken from ref. [64])

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- Interactions via elastic strain fields. It is found that vertical correlation occurs only when the surface is parallel to the elastically hard direction such that the strain energy is minimum exactly above the buried island. Otherwise, the energy minimum will be laterally displaced, especially when the surface orientation is parallel to an elastically soft direction. This central minima will be divided into several energy minima on the next layer (**Fig 2.3j** – (a) and (b)).
- Presence of a non-planar corrugated surface. The reaction of the dot nucleation will depend on the dominating surface mass transport mechanism. Dot nucleation will occur preferentially at the concave surfaces if the surface mass transport during the growth of the wetting layer is dominated by capillary forces due to accumulation of growth species at the concave region. On the other hand, dot nucleation will occur at the top or edges of the surface mound if the surface mass transport is stress-driven surface diffusion – it is expected that the strain at the top of the mound to be minimum compared to the concave region.
- Lateral chemical compositional variation. The lateral chemical composition in the spacer layer may induce a chemical composition modulation as well as a variation in the spacer layer lattice constant, resulting in a lateral variation in the strain on the surface of growth for the next layer of QDs and thus anti-correlation.

Other possible reasons for the anti-correlation can be the thickness of the spacer layer. Shchukin *et al.*, 1999, modelled this anti-correlation as [65]:

Fig 2.3k: Strain field related to thickness of spacer layer (taken from ref. [65])

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$$E_{elastic}^{(SB)} = \frac{h^B}{A_0} \sum_{k_{\parallel}} \left| \tilde{\Theta}(k_{\parallel}) \right|^2 \exp(ik_{\parallel} R_0) (\Delta \tau_{\alpha\beta}) a_{lm} \times \nabla'_m [\nabla_{\alpha} \tilde{G}_{\beta l}(k_{\parallel}; z, z') + \nabla_{\beta} \tilde{G}_{\alpha l}(k_{\parallel}; z, z')] \Big|_{\substack{z=0 \\ z'=-z_0}}$$

where, R_0 is the relative sheet of the two arrays

h^B is the thickness of the buried islands

$\nabla_x \equiv ik_x$, $\nabla'_x \equiv -ik_x$, $\nabla_y \equiv ik_y$, $\nabla'_y \equiv -ik_y$, $\alpha, \beta = 1, 2$ and $l, m = 1, 2, 3$

$\tilde{G}_{il}(k_{\parallel}; z, z')$ is the static Green's tensor

Thus far, no conclusion has been made on the formation of QD except that there is a general diffusion-bias trend in its growth. Some theories have been put forth with regard to the formation of QDs as the breaking of the thin film. However, this is found to be unsatisfactory as it means dislocation formation or cracking and contradicts other observed processes such as the Ostwald ripening process. In addition, these theories are based on continuum view point and may have serious failings compared to the atomistic approach. Hence there is a need to develop atomistic techniques to study QD growth in order to derive a general theory of its formation, regardless of the material used.

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2.3.3 Gallium Nitride (GaN) Quantum Dots

For GaN quantum dots, the literature reveals that 5 different growth process had been established:

- Stranski-Krastanov (SK) either with [41,44] or without surfactants [40,48,66,67] – MBE
- SK mode using ‘anti-surfactants’ [39,46,68] and without [47,48,69] – MOCVD.
- Vapor-liquid-solid approach (VLS) initiated by *Hu et al.* [70,71] – (Gas-source MBE) . This approach involves first a deposition of Ga droplets on the substrate surface follows by a nitridation process. The residual Ga droplets are then desorbed by increasing the temperature.
- Volmer-Weber (VW) by Degave *et al.* [72,73] – for large lattice mismatched systems using MOCVD.

With the exception of QDs via SK growth mode, the quantum dots grown have been reported to have various deformations. In particular, stacking faults have been reported in both VLS and VW approaches, with existing thread dislocations being reported in the VW approach. GaN QDs grown from the VLS method are reported to be coherent when they are sufficiently small at ~ 5 nm in width, but the amount of stacking faults become predominant with increasing size. Part of the QD seems to be of zincblende structure, rather than maintaining the wurtzite structure throughout. This gives rise to the question of whether the QD may be seriously affected by certain driving forces in the VLS approach.

With regards to VLS, there is another additional problem, in which Al or Si surfactants are able to dissolve in the Ga droplets (AlN and SiC being the common buffer layer or the substrates used for GaN). This will cause further implications and contaminants during the formation of the quantum dots. At present, *Hu et al.* [74] are working on ways to remedy the situation and to allow for better control of this contamination.

In the VW approach, the GaN QDs initially nucleate coherent cubic islands (zincblende), until their size increases, in which some of the QDs are reported to

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exhibit hexagonal structure (wurtzite). The stacking faults found by Degave *et al.* are typically occurring towards the top of the island. From the understanding of GaN thermo-stability (wurtzite GaN is the most thermally stable structure), this is not a surprising finding. Further investigation is needed to solve this stacking fault formation before the VW method is proven feasible for growth of cubic GaN QDs.

The QDs grown by SK mode are the only GaN islands achieved where no stacking faults have been reported, except that there seem to be a preference of nucleating in the vicinity of dislocations and that some of these dislocations (threading edge dislocation) propagate throughout the QD. The possibility of these structural defects acting as elastic potential minima on the growing surface has been suggested Daudin *et al.* [40]. The QDs were also tested to have no dislocation using a Burger circuit. There is also a report by Huang *et al.* [75] that buffer layers of GaN quantum dots can actually reduce the dislocation concentration in the GaN thin film grown from about $\sim 10^{10}$ (typical dislocation density obtained with AlN buffer layer) to $3 \times 10^7 \text{ cm}^{-2}$.

In addition, GaN QDs are shown to be very different from other QDs in several aspects. Gallium itself is an anti-surfactant in the growth process. One of the general theories of QDs is that QDs are formed to reduce the strain energies and hence involved a reconstruction to ease this surface strain. Gogneau *et al.* [44] reported that no QDs were formed if excess gallium is deposited and that the 2D to 3D transition is only observed when the gallium layer had been desorbed. This poses an interesting question of how the QDs are formed and whether it involves the breaking of bonds and diffusion to obtain this 3D transition or other possible mechanisms.

It is believed that there could be other factors that might have been neglected in the observations by Gogneau *et al.* [44]. Firstly, Ga adatoms have a higher sticking coefficient compared to N and hence there is a need to maintain a rich N-condition for growth and cooling. There could also be the possibility that the Ga adatoms do not readily desorb unless there is a deficiency in Ga concentration. Brown *et al.* [67] had suggested that the N adatoms may be able to diffuse rapidly within the layer, which might be critical to island formation. A possibility suggested hereby is that the QDs are actually formed within a region of loosely collected Ga adatoms but the RHEED is

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unable to show this transition due to this layer of Ga atoms collecting on top of the islands.

Gallium has a low melting temperature (300 K) and it is a liquid at room temperature. It is difficult to explain how a liquid could form a layer with sufficient energy to inhibit the formation of QDs. Of course, there could be other possibilities like the desorption process of excess Ga layers which may have given rise to sufficient energies for the reorganization of the Ga and N atoms to form QDs. The actual formation of GaN QDs with excess Ga deposited is currently still unexplained and research efforts may be required into developing new techniques for *in situ* monitoring of QDs growth before this phenomenon can be explained.

Another peculiarity of GaN QDs is its sensitivity to the growth conditions. For example, if its Ga cell temperature is raised 1 K above 922 °C, FM mode may be the predominant growth mode and no QDs are formed [44]. Its sensitivity to the growth conditions can also be extended to the understanding of the energies required for the formation of either zincblende or wurtzite structures as seen in the growth of cubic GaN QDs by SK mode as reported by Daudin *et al.* [40]. This sensitivity is not observed in other QDs mainly because they do not exhibit polytypism characteristics. However, these characteristics can actually aid the understanding of the main controlling growth mechanisms in QDs, and the conditions at which higher energies will result and hence formation of zincblende structures in QDs. Conversely, it will reveal the conditions that will cause lower energies and hence formation of stable wurtzite structures. It is foreseen that the growth mechanisms for cubic GaN QDs may require different conditions at different growth stages in order for successful growth.

Overall, the GaN QDs pose many new problems that have not previously been observed in the growth of other III-V semiconductor QDs. Intense research efforts will therefore be required before its potential can be tapped for the various opto-electronic and electronic applications.

CHAPTER 3

ATOMISTIC SIMULATION TECHNIQUES

3.1 General Overview

In general, there are two main classes of atomistic simulation: deterministic approach – molecular dynamics (MD), and, stochastic approach – Monte Carlo (MC). In addition, there are various hybrid methods developed that adapt certain working principles of MC and MD. A brief description of some of the various atomistic methods developed is as follow:

MD – Molecular Dynamics

The basic idea of MD is that the atoms in a system are treated as particles and their interacting behaviours are governed by a potential function. The potential function relates the bond energy (U) of the atoms with respect to their inter-atomic distances (r). Typically, the potential function is divided into two parts: long-range and short-range. The long-range potential denotes the physisorption or the van der Waals' interaction of the atoms. On the other hand, the short-range potential describe the chemisorption or the behaviour of bonded atoms.

By the differentiation of the potential with respect to the inter-atomic distance (dU/dr), the forces acting on the respective atoms can be obtained. With the availability of the forces (F) and hence accelerations ($a = F/m$, m : mass), the atoms' motions are then obtain by applying Newton's equation of motion.

A basic schematic of MD is as follows:

- 1) Assign atoms' positions and initial velocities
- 2) Run n number of loops
 - i. Compute the forces acting on each atom and the respective accelerations
 - ii. Use Newton's equation of motion to integrate the new positions and velocities
 - iii. Apply Minimization
 - iv. Compute the properties required

Fig 3.1a: Schematic of MD

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Although the principle of MD is simple and clear, there are some associated problems. One of main MD problems is that the accuracy of the simulation depends on how well the potential function is able to describe the atomic interactions. In fact, there is no single formulation of potential function that can describe the full atomic behaviour. There are some forms that are said to display the “proper” atomic behaviour better than others: e.g. Lennard-Jones potential for van der Waals’ interactions and Coulombic potential for ionic particles. However, most atomic interactions are not so simple, i.e. pure covalent, pure ionic or pure van der Waals. Despite the current development in this area of research, the potential function developed is only able to describe accurately some properties under limited conditions.

In addition, the simulation is also dependent on the integrating algorithms of the Newton’s equation of motions. The small time-step sizes (typically of femtoseconds) have to be carefully selected to ensure that the accumulative errors caused by these integrating algorithms will not destabilize the simulation. Equilibration runs are usually performed prior to actual simulation to check for such error and to ensure that the simulated system has stabilized under the imposed conditions – temperature, pressure, *etc.*

The small time-step sizes and potential function used also result in some implications for MD in that the simulations are easily trapped at certain local minimum. This means that the simulation obtained is only one of the possible results and that the whole range of possibilities have not been sampled. Another problem of MD is that it is very computationally expensive despite the availability of supercomputers. Consequently, MD simulation is limited to a maximum physical time of around nanoseconds and an atomic size of a few thousands.

MC – Monte Carlo

The main principle of MC is that an atom(s) is randomly selected and moved at each step. The acceptance or rejection on the move is based on the resulting total energy of the system. According to thermodynamic principles, the system will try to move in the direction of lower energy. There are various acceptance/rejection criteria developed and the most popular is the Metropolis algorithm [76] :

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$$\text{Acceptance} = \min(1, e^{-\beta[U(r_{\text{new}}) - U(r_{\text{old}})])} \quad (3.1.1)$$

$$\text{Where, } \beta = 1/kT, T \text{ is the temperature of the system} \quad (3.1.2)$$

A basic schematic of a Metropolis MC is:

For a predefined n number of loops

- 1) Randomly select an atom in the system
- 2) Displace the atom randomly in space: $r_{\text{old}}(x, y, z) \rightarrow r_{\text{new}}(x', y', z')$ (random walk)
- 3) Compute the new energy of the system, U_{new}
- 4) Accept the new coordinates with the Metropolis scheme.

Fig 3.1b: Schematic of MC

There are several different types of MC simulations. A few of the more commonly-used MC methods are listed:

- *Markov Chain MC* [77]

This type of MC is actually a Metropolis MC which uses the Metropolis algorithm to generate a sequence or chain of events, independent of the previous or initial coordination.

- *Off-Lattice MC*

This MC uses potential function to move its atom and in the computation of the new system energy. Hence, instead of shifting from one predefined fixed site to another, moves outside these considered positions can be made.

- *Kinetic MC*

In Kinetic MC, a list of predicted moves and their respective rates of occurrence is made prior to the run. A randomly selected atom is then displaced by a move, randomly chosen from this list.

For most MC simulations, only one atom is being selected and moved at each MC step. The main reason is that there is a higher possibility of rejection with increasing number of atoms moved. In MC, the typical acceptance rates in the range of 10% to 30%, which means that most of the MC steps run are rejected – a waste of computational resources. Hence, it is important to maintain relatively high acceptance rates and single atom move is encouraged [78].

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Unlike MD, MC is able to simulate a much larger system of a few hundred thousand atoms for a longer physical time range of up to a few seconds. In addition, MC moves can avoid the trapping within local minima with the proper setting. However, it faces limitation and issues of accuracy as in MD: the results are governed by the input such as the predefined list used in KMC or potential functions applied in off-lattice MC. In other words, more information is required for MC simulations compared to MD, which requires only the inter-atomic interaction described by the potential function.

In addition, MC depends heavily on the random number generators. Despite the name “random number generator”, these generators may not produce truly random numbers, especially for a small sample. This is a serious problem as “un-random” numbers produced may cause a bias in the final results [79].

Another major problem faced by MC is the random walk, whereby a selected atom is moved to a position of an existing atom in the system. Although various different schemes of MC have been proposed to solve this problem, the random-walk remains a problem at varying degrees for different schemes since the aim of MC is to allow sampling from a global range of results.

Hybrid MC

As the name implies, this atomic method is a combination of MC and MD methods and was first introduced by Duane *et al.* [80]. The difference with the pure MC method is that HMC uses MD runs to propagate the atomic motions. In other words, all the atoms are moved using MD approaches at each MC step.

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A simplified HMC schematic is as follows:

Fig 3.1c: Schematic of HMC

The Metropolis algorithm can be used as the rejection criteria.

The advantages of HMC over MC and MD are: firstly, problems of random walk in MC are avoided since all the atoms are moved simultaneously according to the potential function. Secondly, HMC is less sensitive to the accumulative numerical errors than MD as the momentums of the atoms are reset at every MC step such that the system is made independent of the previous or initial properties as in MC. Next, HMC evolves at a rate much faster than either MC or MD. It is important to note that MC evolves faster than MD based on the simulated physical time to the computational time required. Since HMC propagates the movements of all atoms rather than one atom in MC, it is understandable for this faster evolution rate [81]. However, this faster evolution rate also causes the main problem in HMC – the difficulty of the computation of the simulated physical time.

Forrest *et al.* [81] proposed a sort of calibration of HMC results to similar MD results for the calculation of this physical time. In their simulation of a $20 \times C_{24}$ system, they found that their HMC simulation evolves about 5 to 10 times much faster than MD. However, different simulation would result in different rates and hence independent calibration has to be carried out.

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KMC-MD method

This simulation approach proposed by Jacobson *et al.* [82] can be described as ‘almost’ hybrid MC, which is designed for deposition simulation. Basically, it is a kinetic Monte Carlo (KMC) process which makes use of MD processes during the deposition of adatoms to the substrate surface. MD processes are used to compute the interactions of deposited atoms on the substrate surface during a ‘deposition event’. The KMC approach is used to compute for all other events such as hopping, diffusion, detachment and so on. Typically KMC is used to simulate ‘rare events’ and had the advantages over MD approach, which tends to be ‘trapped’ in the local minima and unable to reach the global minimum position within a short period of time.

3.2 Literature Review on Atomistic Simulation on GaN

With the development of the atomistic simulation techniques, simulation is becoming a popular tool for investigation of atomic-scale phenomena. In particular, simulation has been used as a virtual experimental lab for simulating experiments which are difficult to carry out in reality. This is indeed the situation for GaN.

In general, the simulation work done on GaN can be separated into three categories:

- *ab initio* – generally used for studying atomic charges, surface reconstructions
- MD – used in observation of thermodynamics and mechanical properties, as well as dislocations
- MC – for vapour deposition of thin film under different conditions.

From the trend of the simulation type used for the various areas of study, it can be seen that the *ab initio* studies are performed on smaller systems and usually when there are insufficient information from experiment. For example, different surface reconstructions have been observed on RHEED during the growth of GaN thin films. Since the RHEED patterns do not allow the differentiation of the atom types, *ab initio* calculations are made to estimate the energies of the atoms in the different configurations so as to predict the atom type responsible for these patterns. Although *ab initio* simulations are by no means meant to replace actual experiments, the results provide an insight into the energies and bonding of the atoms. This allows for some

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interpretation of the experimental observations and enhances our understanding of the underlying physical phenomena.

Another example of the importance of *ab initio* simulations is the proof of a laterally contracted metallic Ga bilayer on the GaN (0001) surface by Northrup *et al.* [83]. They computed different configurations of excess Ga atoms stabilizing on the surface and proved the incommensurate Ga bilayer to be energetically favourable. **Fig 3.2a** shows the atomic structure of the Ga bilayer.

Fig 3.2a: Laterally contracted Ga bilayer model (taken from ref. [83])

Neugebauer *et al.* [84] proposed and demonstrated via the density-functional theory (an *ab initio* principle) and the scanning tunnelling microscopy (STM) that the diffusion of adatoms via AELD (Adatom Enhanced Lateral Diffusion) within the metallic Ga bilayer may be preferred rather than on top of this layer. This is an important insight as it explains the role of Ga as auto-surfactant and how the metallic bilayer contributes to the smoother growth of better quality GaN compared to that grown under N-rich conditions.

FIG. 2 (color online). Cross-sectional view of the valence charge density for a nitrogen adatom at the stable subsurface site (left) and at the barrier configuration for subsurface diffusion (right). Grey and dark grey (online color: blue) filled circles mark the position of Ga and N atoms, respectively. The balls in the top layer mark In atoms. The numbers give the bond length in Å.

Fig. 3.2b: AELD (taken from ref. [84])

As for MD, the focus of most simulation works is to develop a potential function for GaN which is able to reproduce either *ab initio* or experimental results

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and extended the usage of the potential to other properties, such as thermodynamics, mechanical and dislocation formation. In fact, there are eight different potential functions being developed for GaN. Each of them has been proposed by their respective authors for a particular area of studies. A brief description and the tests being performed are as follows:

- Zapol *et al.* [85] proposed a two-body interatomic potential consisting of a long-range Coulombic part and a short-range part, which takes on an analytical expression of the Buckingham form for atoms i and j .

$$U_{ij} = Ae^{(-r_{ij}/\rho)} - Cr_{ij}^{-6} \quad (3.2.1)$$

where, r_{ij} : distance between atom i and j

A, ρ, C : constant potential parameters

The potential has been tested for structure stability – the force field is able to model correctly the wurtzite and zincblende structures of GaN. Testing of the phase transitions, native intrinsic defects due to impurities and zincblende surface relaxation were also carried by the authors.

- Matsumura *et al.* [86] designed a partial ionic two-body potential for GaN and InN to reproduce their lattice constants and phonon frequencies. They fitted their parameters to the results obtained from optical phonon energies measurements.

$$U(r_{ij}) = \frac{Z_i Z_j e^2}{r_{ij}} + k_0(b_i + b_j) \exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) \quad (3.2.2)$$

where, Z_i, Z_j : the atomic charge on atom i and j

r_{ij} : distance between atom i and j

a_i, a_j, b_i, b_j : curve-fitting parameters

k_0 : constant

They performed thermodynamic tests and their results show that GaN is stable up to a temperature of 1300 K.

- Boucher *et al.* [87] developed an empirical, total-energy tight-binding model for GaN. The parameters in the potential are fitted to experimental data of bulk material (elastic stiffness constant) and theoretical data for native point defects.

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$$E_{total} = U(r_{ij}) + E_{bs}(r_{ij}) \quad (3.2.3)$$

$$\text{where, } U(r_{ij}) = \phi_1 e^{[(R_0 - r_{ij})/\alpha]} + \phi_2 \frac{R_0}{r_{ij}} \quad (3.2.3a)$$

$$E_{bs} = \sum_i n_i \epsilon_i, \quad (3.2.3b)$$

ϵ_i : energy eigenvalue of the i th energy level, and,

n_i : corresponding electron occupancy

r_{ij} : distance between atom i and j

$\phi_1, \phi_2, R_0, \alpha$: constant potential parameters

- Wang *et al.* [88] had proposed a model based on Ewald summation algorithm and Keating potential model to compute the long-range Coulomb interaction and the short-range bonding force. The Keating interaction is deduced from the elastic stiffness constant. The potential is used to examine the formation energy of the IDB in GaN.

$$U_i = \left(\frac{1}{2} \sum_{j, j \neq i} \frac{Z_i Z_j}{r_{ij}} \right) + \left[\frac{1}{2} \alpha \left(\frac{3}{4r_0^2} \right) \sum_{i=1}^4 (r_i \cdot r_i - r_0^2)^2 + \frac{3}{4r_0^2} \beta \sum_{i,j>i}^4 (r_i \cdot r_j + \frac{1}{3} r_0^2)^2 \right] \quad (3.2.4)$$

where, r_{ij} : distance between atom i and j

Z_i, Z_j : charges on atoms i and j

α, β, r_0 : constant potential parameters

- Aïchoune *et al.* [89] proposed a “modified Stillinger-Weber” potential function for GaN [89]:

$$U(1, \dots, N) = \sum_{i < j} v_2(i, j) + \sum_{i < j < k} v_3(i, j, k) \quad (3.3.4)$$

$$\text{where, } v_2 = \epsilon A (B r_{ij}^{-4} - 1) e^{[(r_{ij} - a)^{-1}]}, r_{ij} = \frac{d_{ij}}{\sigma} \quad (3.2.4a)$$

$$v_3 = \epsilon \lambda e^{[\gamma(r_{ij} - a)^{-1} + \gamma(r_{ik} - a)^{-1}]} [\cos \theta + \frac{1}{3}]^2 \quad (3.2.4b)$$

$\epsilon, \sigma, A, B, a, \gamma, \lambda$: constant potential parameters

in which the interactions of Ga-Ga, N-N and Ga-N are distinguished. The experimental data of the elastic stiffness constants are used in their parameterization. The main investigation of their potential is to determine the formation energy of the IDB.

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- Bere *et al.* [90] modified the SW potential parameters developed by Aïchoune *et al.* [88] to improve its generalized applicability and the potential takes the same form.
- Nord *et al.* [91] proposed an analytical bond-order potential based on the Tersoff-Brenner form, where the total potential energy is written as a summation of the individual bond energies.

$$U = \sum_i U_i = \frac{1}{2} \sum_{i \neq j} V_{ij} \quad (3.2.5)$$

$$\text{where, } V_{ij} = f_c(r_{ij})[A_{ij} \exp(-\lambda_{ij} r_{ij}) - b_{ij} B_{ij} \exp(-\mu_{ij} r_{ij})] \quad (3.2.5a)$$

$$f_c(r_{ij}) = \begin{cases} 1, r_{ij} < R_{ij} \\ \frac{1}{2} + \frac{1}{2} \cos \left[\frac{\pi(r_{ij} - R_{ij})}{(S_{ij} - R_{ij})} \right], R_{ij} \leq r_{ij} \leq S_{ij} \\ 0, r_{ij} > S_{ij} \end{cases} \quad (3.2.5b)$$

$$b_{ij} = (1 + \beta_{ij}^{n_{ij}} \zeta_{ij}^{n_{ij}})^{-\frac{1}{2n_{ij}}} \chi_{ij} \quad (3.2.5c)$$

$$\zeta_{ij} = \sum_{k \neq i, j} f_c(r_{ik}) g(\theta_{jik}) \omega_{ik} \quad (3.2.5d)$$

$$g(\theta_{jik}) = 1 + \frac{c_{ij}^2}{d_{ij}^2} - \frac{c_{ij}^2}{d_{ij}^2 + (h_{ij} - \cos \theta_{jik})^2} \quad (3.2.5e)$$

$A_{ij}, B_{ij}, \lambda_{ij}, \mu_{ij}, R_{ij}, S_{ij}, n_{ij}, \beta_{ij}, \omega_{ij}, \chi_{ij}, c_{ij}, d_{ij}, h_{ij}$: constant parameters

The parameters for the potential are fitted independently for Ga-Ga, N-N and Ga-N interactions. Firstly, the pair-like terms are deduced by the dimer properties, followed by a fitting to the elastic moduli and other structural properties.

- Harafuji *et al.* [92] developed a two-body interatomic potential consisting of the long-range Coulomb interaction, the Gilbert-type short-range repulsion, the covalent bonding and covalent repulsion of the modified Morse type, as well as the van der Waals interaction:

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$$U_{ij} = \frac{Z_i Z_j e^2}{4\pi\epsilon_0 r_{ij}} + f_0(b_i + b_j) e^{\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right)} + D_{1ij} e^{(-\beta_{1ij} r_{ij})} + D_{2ij} e^{(-\beta_{2ij} r_{ij})} - \frac{c_i c_j}{r_{ij}^6} \quad (3.2.6)$$

where, Z_i, Z_j : charges on atom i and j

e : electrical charge on one electron

ϵ_0 : dielectric constant

$b_i, b_j, a_i, a_j, D_{1ij}, D_{2ij}, \beta_{1ij}, \beta_{2ij}, c_i, c_j$: constant potential parameters

The *ab initio* results for the lattice energy were used in their parameterization. Structural properties such as elastic constant, phonon spectrum formation energies for vacancies were tested by the authors for reliability. This potential has been mainly used to estimate the melting temperature of GaN.

- Zhang *et al.* [93] applied a lattice inversion procedure to derive their potential function for AlN, GaN and InN from pseudopotential total-energy curves of the rocksalt, zincblende and wurtzite structures.

$$U_{ij}(r_{ij}) = \frac{Z_i Z_j}{4\pi\epsilon_0 r_{ij}} + \phi_{ij}^{SR}(r_{ij}) \quad (3.2.7)$$

where, Morse type: $\phi_{ij}^{SR}(r_{ij}) = D\{\exp[-\gamma(\frac{r_{ij}}{R} - 1)] - 2\exp[-\frac{\gamma}{2}(\frac{r_{ij}}{R} - 1)]\}$ (3.2.7a)

Repulsive-exponential type: $\phi_{ij}^{SR}(r_{ij}) = D\exp[-\gamma(\frac{r_{ij}}{R} - 1)]$ (3.2.7b)

In their modelling, they allowed for distinct relationships for all III-III, N-N and III-N interaction. The Repulsive-exponential type potential is applied for III-III and N-N interaction while the Morse type is applied for III-N interatomic bonding.

Tests on the bulk properties, phase stabilities and surface relaxations were carried out using their potential functions.

For empirical potential function, discrete values are required for the parameterization. Most often, the *ab initio* results are used, such as in the computation of atomic charges on the Ga and N atoms. However, it is noticed that among the potential functions for GaN, the chosen values used by different authors are different. It is suspected that the discrepancy arises due to the different interpretations of the authors about Coulombic interaction and their analysis approach. A summary of the

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atomic charges assigned and methods used to estimate the charge values by the different authors is as follow:

Authors	Coulomb term	Atomic Charge Assigned, z	Method Used
Zapol <i>et al.</i> [85]	√	1.6	Mulliken population
Matsumura <i>et al.</i> [86]	√	1.65	Optical phonon frequency (wurtzite)
Broucher <i>et al.</i> [87]	-	-	-
Wang <i>et al.</i> [88]	√	1.147	Phonon frequency analysis (zincblende)
Aichoune <i>et al.</i> [89]	-	-	-
Bere <i>et al.</i> [90]	-	-	-
Nord <i>et al.</i> [91]	-	-	-
Harafuji <i>et al.</i> [92]	√	1.15	Screened effective charge
Zhang <i>et al.</i> [93]	√	0.63	Energy difference between Zincblende and Wurtzite

Table 3: Summary of Atomic charges applied in different GaN potentials

However, from all the works done on the potential functions, it is noted that although the Coulombic potential is applied in the long-range, it is also part of the short-range potential. Generally, the short-range potential function can be segregated into the repulsive energy when the atoms are close to one another and the attractive energy when they are sufficiently far apart. In other words, the Coulombic term within the potential functions act as the attractive potential for unlike atoms and repulsive for like atoms. With the issue of the polarization of GaN unresolved, it is difficult to indicate the degree of influence of this Coulombic part, except that it serves more as a repulsive or attractive term within the potential.

Comparate to MD and *ab initio* works, there are much fewer MC works on GaN [94,95]. The implications may be due to the lack of data on GaN for the MC simulations. For example, Wang *et al.* [94] had estimated that the bond energies of Ga-N and Ga-Ga are approximately those for GaAs. In recent studies, such estimations have been shown to be irrelevant since GaN have been reported to display unique

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behaviours from other III-V semiconductors: Ga adlayer structures on GaN(0 0 0 -1) surfaces are more energetically favourable than on GaAs (-1 -1 -1) surfaces [96]. Similarly in the work reported by Mao *et al.*, they observed that one of the main factors leading to error is the uncertain values of the predefined factors applied in their simulation [95].

3.3 Selection of Modelling Methods

From literature and the study of simulation methods, MD or HMC have been proposed for use in the vapour deposition simulations. The main reason for this selection is the lack of data required for MC. MC simulation requires a list of predefined known rates for the accurate simulation. Estimation of these rates may be made but the reliability of the results is questionable. On the other hand, MD has been intensely tested on the different properties of GaN where various potential functions have been proposed and tested for their accuracy with respect to experimental data or *ab initio* results.

HMC is taken as an alternative due to the consideration of the high computational power requirement for MD. It is noted that MD has been used for thin film deposition simulation. In such simulations, one of the dimensions will be reduced so as to lower this computational cost. However, for 3-dimensional structures such as QD, this reduction is not viable. Hence, prior to simulation, tests have to be carried out to access the required computational costs.

3.4 Selection of Potential Function

The transferability of potential functions has always been a key issue in MD. Transferability is defined here as the ability to use a single set of parameters fitted into a potential for simulation of various applications. In other words, there is usually a limited valid window of application for every set of fitted parameters. Therefore it is important to know the properties that are used for the parameterization and to carry out benchmark tests to assess their reliability.

Depending on the requirements or the intended usage, some of the potentials described incorporate the three-body inter-atomic potential as in the Keating potential,

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SW potential and Tersoff potential. For the other potentials, this three-body potential term has either been neglected or it does not serve the purpose of the particular simulation design.

Fig. 3.4a: Strained atomic structure of GaN

For the simulation of quantum dots, this three-body potential component may play an important role due to the strain experienced as a consequence of lattice-mismatched substrate (heteroepitaxy). These atoms are strained in a particular plane and a certain atomic behaviour should be observed such that the atoms are able to achieve equilibrium within the strained state (See **Fig 3.4a**). Hence the ability of the potential function to model the angular-dependency is of great importance.

In this project, the main aim is to simulate the growth process of GaN quantum dots. Among the GaN potentials, the Keating potential fitted by Wang *et al.* [94], SW potential fitted by Bere *et al.* [90] and the Tersoff-Brenner potential fitted by Nord *et al.* [91] are selected as the possible candidates due to their ability to model at least three-body term. The suitability of the potential functions for the simulation are examined as follows:

Firstly, it is important that the potential has been designed for distinct Ga-Ga, Ga-N and N-N interactions. This is of great importance as the vapour deposition involves the deposition of single Ga and N adatoms (single un-bonded atoms) and the modelling has to be considered for the possibly different interactions of the atoms with the substrate. In addition, there might be the possible occurrence of wrong bonds, i.e. Ga-Ga and N-N might be formed within the crystal structure due to vacancies and other dislocation. Most of the potential functions for GaN satisfy this criterion.

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Secondly, strained behaviour is required to be modelled correctly due the lattice-mismatched substrate, AlN. The Keating potential has been found by *Kikuchi et al.* [97] to model the strained behaviour poorly as the size of the modelled system decreases. Thus the recommended potential for MD of quantum dots as proposed is the SW potential over the Keating potential. They found that the simplicity of Keating potential resulted in the under-estimation of the strained behaviour and thus recommend against its use in small systems such as quantum dots.

Next, the accurate energetic description is required for the simulation. GaN is a material that is highly susceptible to dislocation formation and hence it is suspected that dislocations will form during the QD growth. Therefore the potential function chosen should be able to cater for this possibility. Although most of the potentials for GaN have been tested to simulate the defects, SW potential and Tersoff potential are the two potentials that are found to best describe the dislocation structures [98-100]. Both the Tersoff-Brenner potential and SW potential have been designed to test for defects. However, the SW potential by Aïchoune *et al.* [89] and Bere *et al.* [90] are the only potentials that have been intensely used to test for the various faults (IDB, stacking faults, threading edge dislocation) commonly found in GaN [98-100]. Currently, there has been no further investigation into using the Tersoff-Brenner potential developed by Nord *et al.* [91] for other types of faults in GaN besides IDB.

Last but not least, it will be an added advantage if a similar potential has been developed for AlN. The substrate intended for use in the simulation is the AlN. It will be more efficient and accurate if the potential functions used for AlN and GaN are of the same form. Although the energies of different potentials are very similar, there may be some slight deviation in behaviour (forces acting on the atoms). A comprehensive literature search reveal that no Tersoff-Brenner potential has been fitted for AlN. Although Ruterana *et al.* [100] has developed a set of parameters for AlN, the potential function has no distinguishing parameters for Al-Al (N-N interactions have already been developed).

For the above reasons, the “modified SW potential” is chosen as the potential function for this work. However, the SW potential is only for bonded atoms and does not cater for forces beyond its first-neighbours. Hence an additional long-range

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interaction such as the van der Waals force is required for modelling of physiosorption of the adatoms (single atoms) during the deposition and nucleation processes, before they are bonded to the wetting layer atoms to form the quantum dots. The Coulomb interaction can also be considered since the GaN material is more ionic in behaviour than covalent. For this reason, certain modification by the additional of the long-range interaction is required in order to cover the requirements of the problem.

It is important to note that there are disadvantages associated with the SW potential which has been fitted by Bere *et al.* [90]. So far, there is no other reported test of the potential for structural properties such as melting point of the wurtzite structure and the properties of the GaN zincblende structure. The latter can be assumed to be sufficiently examined for reproducibility by the authors as the potential was tested for describing stacking faults energies – stacking faults are due to the violation of the layer stacking rule, i.e. the insertion of the Cc layer in the wurtzite structure sequence AaBbAaBbAaBb. It is important to note that a sequence of AaBbCcAaBbCc.. will result in a zincblende structure in the (1 1 1) direction.

CHAPTER 4

TESTING OF STILLINGER-WEBER POTENTIAL

4.1 Molecular Dynamics (MD)

In general, MD involves 3 stages: initialization, equilibration and simulation. In the initialization stage, basic inputs of the model, such as the atomistic positions of the atoms, initial velocities and forces, are required to 'initialize' the system model. Following this initialization, the system is allowed to relax in the equilibration stage to ensure a stable, consistent system before the system conditions are modified in the simulation process to obtain the required properties and output.

The forces are calculated for each atom in the system after which the new positions and velocities of the atoms are computed by integration of motion. The new forces are then re-computed according to the new positions of the atoms and the iteration continues. Minimization routine is applied at intervals of a prescribed number of cycles so as to ensure that the system is at its minimum energy. To obtain certain properties or behaviour of the system, various conditions are applied to the system. For example, for melting simulation, the temperature of the system is increased continuously at constant pressure. Hence, before applying any of these conditions, knowledge of how such conditions are applied is required.

The following are some of the basic elements of the MD methodology:

Forces

The forces acting on the atoms are obtained from the gradient of the intermolecular potential function governing their behaviour:

$$F_x = -\frac{dU}{dx} \quad ; \quad F_y = -\frac{dU}{dy} \quad ; \quad F_z = -\frac{dU}{dz} \quad (4.1.1)$$

where, ϕ : the intermolecular potential function

F_x, F_y, F_z : forces of the atom in the x, y and z -direction

Derivation of the forces from the SW potential is presented in Appendix A.

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Equation of motions

There are numerous equations of motions used in MD. The motions are integrated from the accelerations, velocities and other possible considerations depending on the algorithm. It is important to note that the acceleration are computed from the forces F_x , F_y and F_z . As the reduced units (See section 4.2 for details) for mass is taken in this project to be such that the mass of N atom is unity, the forces for N atoms are actually the atomic acceleration. Since the mass ratio of Ga atom to N atom is 4.97 to 1.0, the Ga atom's acceleration is obtained by multiplying the force by a factor of (1/4.97).

Among the most common equations used in MD simulations are the Gear's Predictor-Corrector and the Verlet equation.

- Gear's 5th order Predictor-Corrector

$$r_i(t + \Delta t) = r_i(t) + \dot{r}_i(t)\Delta t + \ddot{r}_i(t)\frac{(\Delta t)^2}{2} + r_i^{(3)}(t)\frac{(\Delta t)^3}{3!} + r_i^{(4)}(t)\frac{(\Delta t)^4}{4!} + r_i^{(5)}(t)\frac{(\Delta t)^5}{5!} \quad (4.1.2a)$$

$$\dot{r}_i(t + \Delta t) = \dot{r}_i(t) + \ddot{r}_i(t)\Delta t + r_i^{(3)}(t)\frac{(\Delta t)^2}{2} + r_i^{(4)}(t)\frac{(\Delta t)^3}{3!} + r_i^{(5)}(t)\frac{(\Delta t)^4}{4!} \quad (4.1.2b)$$

$$\ddot{r}_i(t + \Delta t) = \ddot{r}_i(t) + r_i^{(3)}(t)\Delta t + r_i^{(4)}(t)\frac{(\Delta t)^2}{2} + r_i^{(5)}(t)\frac{(\Delta t)^3}{3!} \quad (4.1.2c)$$

$$r_i^{(3)}(t + \Delta t) = r_i^{(3)}(t) + r_i^{(4)}(t)\Delta t + r_i^{(5)}(t)\frac{(\Delta t)^2}{2} \quad (4.1.2d)$$

$$r_i^{(4)}(t + \Delta t) = r_i^{(4)}(t) + r_i^{(5)}(t)\Delta t \quad (4.1.2e)$$

$$r_i^{(5)}(t + \Delta t) = r_i^{(5)}(t) \quad (4.1.2f)$$

The corrector is of the following form:

$$r_i = r_i^p + \frac{3}{16}\Delta\ddot{r}_i \quad (4.1.3a)$$

$$\dot{r}_i = \dot{r}_i^p\Delta t + \frac{251}{360}\Delta\ddot{r}_i \quad (4.1.3b)$$

$$\frac{\ddot{r}_i(\Delta t)^2}{2!} = \frac{\ddot{r}_i^p(\Delta t)^2}{2!} + \Delta\ddot{r}_i \quad (4.1.3c)$$

$$\frac{r_i^{(3)}(\Delta t)^3}{3!} = \frac{r_i^{(3)p}(\Delta t)^3}{3!} + \frac{11}{18}\Delta\ddot{r}_i \quad (4.1.3d)$$

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$$\frac{r_i^{(4)}(\Delta t)^4}{4!} = \frac{r_i^{(4)P}(\Delta t)^4}{4!} + \frac{1}{6} \Delta \ddot{r}_i \quad (4.1.3e)$$

$$\frac{r_i^{(5)}(\Delta t)^5}{5!} = \frac{r_i^{(5)P}(\Delta t)^5}{5!} + \frac{1}{60} \Delta \ddot{r}_i \quad (4.1.3f)$$

$$\text{where, } \Delta \ddot{r}_i = [\ddot{r}_i(t + \Delta t) - \ddot{r}_i^P(t + \Delta t)] \quad (4.1.3g)$$

Δt is the time step used

r_i is the position of atom i

r_i^P is the predicted position of the atom i computed from the predictor

- Velocity Verlet Equation

$$r(t + \Delta t) = r(t) + v(t) + \frac{f(t)}{2m} \Delta t^2 \quad (4.1.4a)$$

$$v(t + \Delta t) = v(t) + \frac{f(t + \Delta t) + f(t)}{2m} \Delta t \quad (4.1.4b)$$

- Multiple Time-scale Algorithm

As the name implies, this algorithm applies two or more time scales. There are various multiple time-scale algorithms developed such as r-RESPA (reversible-Reference System Propagator Algorithm) by Tuckerman *et al.* [101] and TJMTS (Teleman and Jonsson multiple time-step algorithm) by Teleman and Jonsson [102]. Over the years, the r-RESPA has gained popularity and recognition in providing better performance compared to other algorithms. In addition, the RESPA has also been proven to be reversible thus enabling a large range of applications such as in generalized HMC.

There are two main reasons for the need to use multiple time-scales here— firstly, long-range interaction does not change significantly compared to short-range interaction for a small displacement and, secondly, the different vibration frequencies between a heavy and a light atom. In MD, long-range interactions are computationally expensive and time-consuming due to the larger domain considered. Since the changes due to long-range interaction is not significant for small atomic displacements, these interactions can be updated once every few time steps to save computation cost. The multiple time-scale algorithms can assume the

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long-range interactions to be constant as in TJMTS or taken relative to the short-range interaction as in the r-RESPA.

When there is a large disparity in the masses of the atoms, as demonstrated by Tuckerman *et al* [101], and, if the time step used is large, the error accumulation especially for the lighter mass atoms will become increasingly large and this might result in instability. This is not surprising as the lighter particle is expected to have higher velocities and hence higher vibration frequencies. Although the general rule suggested is to apply multiple time-scale algorithms only for atoms whose mass ratio is at least 10, tests on mass ratio of <10 have not been carried out.

The r-RESPA can be mainly classified by 3 types [103]:

- force-based for modeling of system with long-range and short-range interaction

(In Pseudo codes- Using Velocity Verlet)

```

 $v = v + F^{(s)} \Delta t / (2m)$ 
do  $i=1, n$ 
   $v = v + F^{(f)} \delta t / (2m)$ 
   $x = x + v \delta t$ 
  -> Update fast forces
   $v = v + F^{(f)} \delta t / (2m)$ 
enddo
-> Update slow forces
 $v = v + F^{(s)} \Delta t / (2m)$ 

```

Fig 4.1a: Schematic of force-based RESPA

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- particle-based for modeling of system with particles of disparate masses

(In Pseudo codes – Using Velocity Verlet)

$$v_h = v_h + F_h \Delta t / (4m)$$

$$x_h = x_h + v_h (\Delta t / 2)$$

-> Update forces for heavy particles

$$v_h = v_h + F_h \Delta t / (4m)$$

do $i=1, n$

$$v_l = v_l + F_l \delta t / (2m)$$

$$x_l = x_l + v_l \delta t$$

-> Update forces for light particles

$$v_l = v_l + F_l \delta t / (2m)$$

enddo

$$v_h = v_h + F_h \Delta t / (4m)$$

$$x_h = x_h + v_h (\Delta t / 2)$$

-> Updates forces for heavy particles

$$v_h = v_h + F_h \Delta t / (4m)$$

Fig 4.1b: Schematic of particle-based RESPA

- force-based and particle-based for modeling of system with long-range and short-range interaction of particles with disparate masses. Usually more than two different time scales are applied for this algorithm.

Basically, the RESPA involves separation of the force terms into different parts: force for light particles, force for heavy particles, short-range forces and long-range forces. Tuckerman *et al.* [101] applied the Liouville operator on a system of f degrees of freedom, defined in Cartesian coordinates:

$$iL = \{..., H\} = iL_1 + iL_2 = \sum_{j=1}^f \left[\dot{x}_j \frac{\partial}{\partial x_j} + F_j \frac{\partial}{\partial p_j} \right] \quad (4.1.5)$$

and this is followed by using the Trotter theorem,

$$e^{(iL_1 + iL_2)t} = \lim_{m \rightarrow \infty} \left[e^{iL_2 t / (2m)} e^{iL_1 t / (m)} e^{iL_2 t / (2m)} \right]^m \quad (4.1.6)$$

to decompose the force terms. The Trotter theorem is also responsible for making the final propagator reversible.

Periodic Boundary Conditions

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Periodic Boundary Conditions (PBC) is an important technique used in MD to simulate a bulk material using only one cell. It is based on the assumption that the cell simulated is able to depict the behaviour of the whole bulk material. Hence the cell size applied must be sufficiently large and yet not too huge to the extent that unnecessary computation time is required.

Fig 4.1c: Periodic Boundary Condition (PBC)

The above figure shows the behaviour of the PBC. Only the central dark cell is the *True* cell – the actual cell simulated. The mapping of the imaginary cells (cell in a lighter shades) is done by assuming that the atom exiting from one end of the cell will cause another atom to enter into the cell from the opposite side.

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Temperature

The temperature of the system can be computed from the virial equation:

$$\text{Kinetic energy of system} = \frac{1}{2} k_b T \quad (4.1.7)$$

where, k_b is the Boltzmann constant ($= 8.62 \times 10^{-5} \text{ eV/atom-K}$)

Hence, for a 3-dimensional system, the temperature can be calculated as:

$$T = \frac{2}{3Nk_b} K \quad (4.1.7a)$$

where, K is the kinetic energy of the system

N is the number of atoms in the system

Temperature Control by Velocities Scaling

The most simple method to achieve temperature control is by velocities scaling. The desired temperature is maintained by scaling the velocities of the atoms, v_x , v_y and v_z in the system. The factor to scale the velocities of the atoms is:

$$\text{Factor} = T_{\text{desired}}/T_{\text{instantaneous}} = \sqrt{\frac{3 \times N \times k_b T_{\text{desired}}}{\sum_{i=1}^N m \times (v_x^2 + v_y^2 + v_z^2)}} \quad (4.1.8)$$

where, $T_{\text{instantaneous}}$ is the instantaneous System temperature

T_{desired} is

the desired temperature of the system

N is the total number of atoms in the system

m is the mass of the atom

Pressure

In MD, pressure is calculated as:

$$\text{pressure} = \frac{Nk_b T}{V} + \frac{2W}{3V} = \frac{1}{3V} (2K + W) \quad (4.1.9)$$

$$\text{where, } W \text{ is the internal virial (} W = \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N r_{ij} \cdot F_{ij} \text{)} \quad (4.1.9a)$$

T is the instantaneous kinetic temperature (Eqn. 4.1.7)

K is the instantaneous kinetic energy of the system

V is the volume of the system

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Berendsen Pressure Control

In Berendsen pressure control, the changes in the pressure is adjusted by scaling the coordinates of the particles and the size of the unit cell in the periodic boundary conditions. In a way, the system is coupled to a pressure ‘bath’ to maintain the pressure set. The factor to be scaled takes the form:

$$\mu = [1 + \frac{\Delta t}{\tau} \gamma (P - P_0)]^{\frac{1}{3}} \quad (4.1.10)$$

where, Δt is the time step

P is the instantaneous pressure

P_0 is the desired pressure

γ defines the strength of the pressure coupling as well as the compressibility of the system (user-defined)

τ is the relaxation time constant (user-defined)

However, as the crystal structure of Wurtzite is not symmetric in the x , y and z -directions, direct application of the Berendsen scaling factor is not suitable and will cause a distortion of the crystal structure itself. Hence a modification is made as follows:

$$\mu_i = [1 + \frac{\Delta t}{\tau} \gamma (P_i - P_0)] \quad (4.1.10a)$$

where, μ_i is the scaling factor of the positions in the i -direction

P_i is the computed pressure of the computed for the i -direction

In this way, 3 independent scaling factors are obtained for the 3 different directions and are applied to their respective directions in the pressure scaling.

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Translation order parameter

The translation order parameter, λ , is a common method to monitor the dissolution of a crystal.

$$\lambda_x = \frac{1}{N} \sum_i^N \cos\left(\frac{4\pi x_i}{a_x}\right), \quad \lambda_y = \frac{1}{N} \sum_i^N \cos\left(\frac{4\pi y_i}{a_y}\right), \quad \lambda_z = \frac{1}{N} \sum_i^N \cos\left(\frac{4\pi z_i}{a_z}\right) \quad (4.1.11a)$$

$$\lambda = \frac{1}{3} [\lambda_x + \lambda_y + \lambda_z] \quad (4.1.11b)$$

where, a_x , a_y and a_z are the unit lattice parameters in x, y and z -direction

N is the total number of atoms in the system

If a body-fixed frame is preferred over a space-fixed frame, the following modified translation order parameter λ_1 can be used:

$$\begin{aligned} \lambda'_x &= \frac{1}{N} \sum_i^N \cos\left(\frac{4\pi(x_i - x_1)}{a_x}\right) \\ \lambda'_y &= \frac{1}{N} \sum_i^N \cos\left(\frac{4\pi(y_i - y_1)}{a_y}\right) \end{aligned} \quad (4.1.11c)$$

$$\begin{aligned} \lambda'_z &= \frac{1}{N} \sum_i^N \cos\left(\frac{4\pi(z_i - z_1)}{a_z}\right) \\ \lambda_1 &= \frac{1}{3} [\lambda'_x + \lambda'_y + \lambda'_z] \end{aligned} \quad (4.1.11d)$$

where, (x_1, y_1, z_1) is the coordinate of the chosen atom in the system

λ_1 is used when a translation of the system is expected.

The values for both λ and λ_1 will go to zero when the atoms are no longer in any particular order or is in an amorphous state. Hence, it is very useful in monitoring the structure of the atoms as to whether it is still crystalline or amorphous.

It is important to note that the unit lattice parameter, a values in λ and λ_1 will be different in the x, y and z -direction for the wurtzite.:

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$$a_x = a$$

$$a_y = a \cos(30^\circ)$$

$$a_z = c$$

where, a and c are the lattice units for the wurtzite

Boltzmann's H-function

The Boltzmann's H -function is used to monitor the development of the velocity distributions in a system.

$$H(t) = \int_{-\infty}^{\infty} f(v) \ln f(v) dv \quad (4.1.12a)$$

where, $f(v)$ is the velocity distribution at time t .

If the velocity distribution follows the Maxwell distribution, the H -function should vary with temperature only.

For the wurtzite structure, the H -function components should be computed individually in its x , y and z component, that is, for example in the x -direction:

$$H_x(t) = \int_{-\infty}^{\infty} f(v_x) \ln f(v_x) dv \approx \sum_{\Delta v_x} f(v_x) \ln f(v_x) \Delta v_x \quad (4.1.12b)$$

and the total H -function is therefore:

$$H = \frac{1}{3} [H_x + H_y + H_z] \quad (4.1.12c)$$

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4.2 Reduced Units

The SW potential is designed to allow for dimensionless parameterization or reduced units, which involves scaling all parameters used in the simulation. The advantages of these reduced units are: firstly, many combinations of the density, temperature, energy and length do correspond to the same state in reduced units. This is useful in simulation in that we can compare the results of different materials in reduced units. For example, in SW potential, the potential of an atom (be it Si, InAs or GaN) in reduced units actually corresponds to the number of neighbours it has – it will have a potential of around ~ 1.0 for one neighbour bonded and ~ 4.0 for 4 neighbours bonded. Hence in a way, although the actual energies of the atom are different for Si, InAs and GaN, direct observation to the number of neighbours can be made and seen easily by its potential. Secondly, the reduced units will enable the involved quantities to be scaled to a smaller order of -3 to $+3$. This is of particular interest as most of the units dealt in MD can be either very large or very small. This will help avoid overflowing or under-flowing of data.

The following are some of the reduced units used:

$$\sigma - \text{length} = 1.695 \text{ \AA}$$

$$\epsilon - \text{energy} = 2.17 \text{ eV} = 2.17 \times 1.602 \times 10^{-19} = 3.476 \times 10^{-19} \text{ J}$$

$$\tau - \text{time} = 1.39 \text{ ps}$$

$$m - \text{mass} = 2.3255 \times 10^{-23} \text{ g} \quad (\text{mass of one N atom} \approx \text{mass of one Ga atom}/4.97)$$

From the defined basic reduced units, we can obtain values of other reduced units:

$$T - \text{temperature} = \epsilon/k_b = 25174 \text{ K}$$

$$V - \text{velocities} = \epsilon/m = 2.17 \times 1.602 \times 10^{-19} / (2.3255 \times 10^{-23}) = 14948.8 \text{ m/s}$$

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4.3 Heating Simulation

A simple simulation of heating a bulk GaN crystal is conducted, whereby the temperature of the system is increase continuously until the system becomes disordered. The schematic of the program is shown in Appendix B. Each simulation takes about 6 hours on a Pentium IV PC. The purpose of this test is to gauge the thermal stability range of the SW potential. In general, a heating scheme is required for melting simulation – higher heating rate is applied initially while a lower rate is used when approaching the melting point. This is to reduce the computational time involved and to reduce the error in estimating the melting temperature.

Before equilibration, the system is checked via standard reliability tests. The tests to be carried out include:

- Low random initial velocities applied to the atoms throughout the system. The system is then run without velocity scaling.
- The system is then run with the velocities of the atoms are being scaled and maintained.

The following results should be obtained for the above tests:

- The total energy is fluctuating about a constant value during equilibration
- The positional order parameter fluctuates about a certain value with the fluctuations having magnitudes less than $\sqrt{N}/N$, where N is the number of atoms in the system
- The H-function is near a value consistent with the Maxwell velocity distribution.

The program is first tested for reliability first without any temperature control to ensure the codes are correct. The simulated system is a $6 \times 6 \times 6$ lattice units system with 864 atoms. Periodic boundary condition is applied in all (x , y , z) directions. Three different algorithms – Gear's Predictor-Corrector, velocity Verlet and RESPA – are applied separately to the simulation. RESPA is applied such that the time-step size used for computing Ga atoms is twice to that of the N atoms, hence the algorithm is termed as RESPA2 hereby.

Fig 4.3a: Gear’s Predictor-Corrector Reliability Test (Without Temperature Control)

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Fig 4.3b: Velocity Verlet Reliability Test (Without Temperature Control)

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Fig 4.3c: RESPA Reliability Test (Without Temperature Control)

Fig 4.3d: Heating simulation using Gear's Predictor-Corrector – Equilibration

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Fig 4.3e: Heating simulation using velocity Verlet

Fig 4.3f: Heating simulation using RESPA2

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First of all, the heating simulation using Gear's Predictor-corrector was discontinued after equilibration. As observed in **Fig 4.3c**, the properties obtained during the equilibration are fairly unstable even if this trend tends to fluctuate about a certain equilibrium value eventually. Since the reliability tests conducted prior to heating shows that the 3 algorithms are able to reach equilibrium, this instability is attribute to the possible memory effect of the Gear's Predictor-corrector. Although each of these algorithms are different in terms of their energy conservation and accuracy, the simulated bulk GaN system is able to achieve equilibrium.

A slightly different heating scheme is applied to the velocity Verlet and that for RESPA2 as the time-step applied are $dt = 0.002 \tau$ and $dt = 0.01 \tau$ respectively. A larger time-step applied would mean that the accumulative numerical error increases as well. To prevent system instability due to this accumulative error, a more gradual heating scheme is applied to the simulation using RESPA2.

The thermal stability point is determined when the Order parameter approaches and start fluctuating about zero. The thermal stability range for the simulations using the velocity Verlet and RESPA2 are approximately 2000 K and 1930 K respectively. Both algorithms give very close values as the thermal stability range is determined by the SW potential function. The slight deviation may be caused by numerical accumulation errors or that the different heating schemes applied may have resulted in a deviation of the estimated value.

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4.4 Melting Simulation

There are several methods for simulating the melting process, which involved either single phase or multi-phases. The single phase melting method is applied here and the schematic is similar to that of the heating simulation in Section 4.3. The method applied is similar to that done by Nord *et al.* [91], in which only pressure and temperature control schemes are involved. Throughout the process, the system is maintained at a constant pressure but its temperature is slowly increased for every fixed number of loops run.

Before the system is set for the melting, it is equilibrated at the pressure used for the melting simulation at an initial temperature. This initial temperature applied must be within the thermal stability range of the SW potential function to ensure for stability. From the heating test, the SW potential is able to be thermally stable up to ~ 1950 K. However, with the involvement of pressure, it is unforeseeable whether the melting point would be greater or lower than the thermal stability range. Hence the temperature of 300 K, similar to the starting temperature applied for the heating simulation, is selected to start the melting.

To maintain the temperature and pressure of the system, velocities scaling and Berendsen pressure control schemes are chosen and applied for their efficiency and simplicity (See *Chapter 4.1* for details). Before the Berendsen pressure control can be applied, an ideal value for γ must be first defined. As γ is related to the compressibility of the system and solids have in general low compressibility, low values of γ should be used. To understand and appreciate the range of low values of γ , tests have been carried out with γ values having as high as 10 in which the GaN becomes highly sensitive to pressure. Although equilibrium is reached very quickly, there is a serious distortion of the wurtzite structure. To prevent distortion to the structure, a smaller range of $(0.01 \sim 0.05)$ is selected for testing. During the testing, no velocities scaling is applied.

Since both velocity Verlet and RESPA2 give similar results in the heating simulations, it is assumed that the algorithms are similar in behaviour. Hence only velocity Verlet is applied for the melting simulation.

Fig 4.4a: Equilibration Results for $\gamma = 0.005$

Fig 4.4b: Equilibration Results for $\gamma = 0.004$

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Fig 4.4c: Equilibration Results for $\gamma = 0.003$

Fig 4.4d: Equilibration Results for $\gamma = 0.002$

Fig 4.4e: Equilibration Results for $\gamma = 0.001$

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It is found that the simulation time to reach equilibrium increases with lower γ values. In fact, the effect of the pressure is too small when $\gamma = 0.001$ that the system has not reached equilibrium even after 50,000 loops. If the system is unable to reach equilibrium sufficiently fast, this might cause error or instability during the melting simulation whereby the temperature is set to increase at a certain rate. Based on these considerations, a suitably low value of 0.004 is applied for γ .

It is to be noted that the value of the order increases when the pressure drops. As the pressure drops, the bulk GaN system expands in size and hence increases the atomic spacing of the atoms, resulting in an increase of the order magnitude. It is by no means that the decrease in pressure resulted in a more organized atomic structure in this case.

Equilibration is carried out at $\gamma = 0.004$ at the temperature of 300 K and pressure of 1 atm for 40,000 loops, which is observed to be sufficient for the system to reach equilibrium. The heating scheme applied after the equilibration: an increment of 20 K every 1000 loops until 1500 K, follows by an increment of 10 K every 1000 loops.

Fig 4.4f: Heating Scheme applied to the melting simulation

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Fig 4.4g: Results for melting of bulk GaN

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Fig.4.4g shows the properties during the melting process. From the results, it is estimated that the melting point is around 2050 K whereby GaN turns from solid phase to liquid, resulting in the oscillating value around zero as shown in the order property.

The melting test of GaN is experimentally difficult to conduct due to the need to maintain a high equilibrium pressure of nitrogen (around 60 kbar) over GaN, otherwise formation of gallium droplets will be resulted on the surface of GaN. Experimentally, GaN is found to be thermally stable at 1343 K and 1 atm pressure [99].

The simulated melting temperature by Harafuji *et al.* [94] for single-phase simulation is approximately 3200 K at 1 atm pressure. Nord *et al.* [91] have carried out similar single-phase melting simulation and have obtained the melting point to be 3500 K at 45 katm pressure. So far in the literature, the reported melting temperature ranges from 1973 K to 2573 K and that the estimated melting point would increase with the pressure. Although the simulated melting point is much lower than the values obtained by different GaN potential, the simulated result at 2050 K is found to be closer to the estimated melting point in literature. Hence SW potential is tested to be suitable and stable for conditions (typically > 700 °C) applied for the vapour deposition of GaN for QD growth.

CHAPTER 5

PRELIMINARY TESTS

FOR VAPOR DEPOSITION SIMULATION

Prior to the actual vapor deposition simulation, two tests are designed and conducted –relaxation of adatoms and impact test. The first test is intended to examine the time-step range suitable for use in the vapor deposition simulation with respect to the algorithm employed. The second impact test is designed to investigate the thickness of the substrate in terms of the number of atomic layers required to simulate a bulk substrate.

The main purpose of these tests is to gauge the possible computational cost for the vapor deposition simulation. Although the MD method has been used for such vapor deposition simulations [104], the greatest limitation to this method is its requirement of high computational power. In particular, for the simulation of QD growth in this project, this cost cannot be lowered by reducing the dimensional order as in thin film growth as QD is 3-D growth process whereas thin film is only 2-D.

5.1 Deposition Test

This test is designed to deposit a mixture of N and Ga adatoms onto a substrate at random locations. The substrate atoms are fixed in their positions throughout the simulation. This design is to simplify the interaction of the adatoms with the substrate atoms. Since the substrate atoms are taken to be fixed, only one lattice unit thickness is applied in the z-direction. The potential applied is the SW potential, without any modification or long-range term added. Three different integrating algorithms – velocity Verlet, Gear's 5th order predictor-corrector and r-RESPA – are tested and assessed for their suitability.

Observations

In first test, the range of suitable time-step from 0.001τ (~ 1 fs: typical time-step size used in MD) to 0.1τ (~ 0.1 ps: typical time-step size used in HMC) will be analyzed. To avoid the complexity of the substrate atoms interaction with the adatoms,

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the substrate atoms are kept fixed. Velocity verlet algorithm, Gear's predictor-corrector and r-RESPA are used for the testing.

It is found that the Gear's predictor-corrector is unstable when the time-step increases beyond 0.02τ and the adatoms fail to stabilize at the predicted equilibrium height. Rather, at 0.01τ , the adatoms seem to form a gaseous layer on top of the substrate surface. Similar observations are made for vRESPA.

Of the three algorithms, only the velocity Verlet is able to allow the adatoms to settle quickly onto the substrate at the equilibrium height when a sufficiently large time-step range of $0.05 \sim 0.18$ is used. For smaller time-step sizes, similar problems are encountered as with the vRESPA and Gear's predictor-corrector.

To investigate if the results obtained is attributed to some programming errors, the potential energy surface (PES) described by the GaN SW potential is examined for different surfaces (N-terminating and Ga-terminating) of GaN (0 0 0 1) or Ga-polarity with respect to Ga and N adatoms.

PES Examination

The range of heights tested is from 1.8σ (the maximum cut-off distance) to close to the substrate atoms position of 0.7σ . The surface examined is a 2×2 ($x \times y$) surface, Ga-polarity, with PBC (See Section 4.1 for details) applied in the xy -plane. The extended surfaces are shown in **Fig 5.5a** and **Fig 5.1d**. The PES are sampled at 50×50 points in the xy -plane.

Fig 5.5a: N-terminating surface examined

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Fig 5.1b(i): GaN PES for N-terminating surface, Ga adatom $Z = 1.7$

Fig 5.1b(ii): GaN PES for N-terminating surface, Ga adatom $Z = 1.5$

Fig 5.1b(iii): GaN PES for N-terminating surface, Ga adatom $Z = 1.4$

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Fig 5.1b(iv): GaN PES for N-terminating surface, Ga adatom Z = 1.3

Fig 5.1b(v): GaN PES for N-terminating surface, Ga adatom Z = 1.2

Fig 5.1b(vi): GaN PES for N-terminating surface, Ga adatom Z = 1.15

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Fig 5.1b(vii): GaN PES for N-terminating surface, Ga adatom Z = 1.1

Fig 5.1b(viii): GaN PES for N-terminating surface, Ga adatom Z = 1.0

Fig 5.1b(xi): GaN PES for N-terminating surface, Ga adatom Z = 0.9

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Fig 5.1b(x): GaN PES for N-terminating surface, Ga adatom $Z = 0.8$

Fig 5.1b(xi): GaN PES for N-terminating surface, Ga adatom $Z = 0.7$

The GaN PES for Ga-terminating surface with N-adatom are not shown as the polarity is maintained and hence the PES are assumed to be similar to that of N-terminating surface with Ga-adatom.

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Fig 5.1c(i): GaN PES for N-terminating surface, N adatom Z = 1.4

Fig 5.1c(ii): GaN PES for N-terminating surface, N adatom Z = 1.3

Fig 5.1c(iii): GaN PES for N-terminating surface, N adatom Z = 1.2

Fig 5.1c(iv): GaN PES for N-terminating surface, N adatom Z = 1.1

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Fig 5.1c(v): GaN PES for N-terminating surface, N adatom Z = 1.0

Fig 5.1c(vi): GaN PES for N-terminating surface, N adatom Z = 0.9

Fig 5.1c(vii): GaN PES for N-terminating surface, N adatom Z = 0.8

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Fig 5.1c(viii): GaN PES for N-terminating surface, N adatom Z = 0.7

Fig 5.1c(ix): GaN PES for N-terminating surface, N adatom Z = 0.6

Fig 5.1c(x): GaN PES for N-terminating surface, N adatom Z = 0.5

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Fig 5.1c(xi): GaN PES for N-terminating surface, N adatom Z = 0.4

Fig 5.1d: Ga-terminating surface examined

Fig 5.1e(i): GaN PES for Ga-terminating surface, Ga adatom Z = 1.6

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Fig 5.1e(ii): GaN PES for Ga-terminating surface, Ga adatom Z = 1.5

Fig 5.1e(iii): GaN PES for Ga-terminating surface, Ga adatom Z = 1.4

Fig 5.1e(iv): GaN PES for Ga-terminating surface, Ga adatom Z = 1.3

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Fig 5.1e(v): GaN PES for Ga-terminating surface, Ga adatom Z = 1.2

Fig 5.1e(vi): GaN PES for Ga-terminating surface, Ga adatom Z = 1.1

Fig 5.1e(vii): GaN PES for Ga-terminating surface, Ga adatom Z = 1.0

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Fig 5.1e(viii): GaN PES for Ga-terminating surface, Ga adatom $Z = 0.9$

From these PES diagrams, a few conclusions can be made. Firstly, the minimum energy positions are different at various heights. Secondly, at certain height range, the minimum energy positions shifted very quickly. This range is observed at around 1.0σ to 1.1σ for Ga-N interaction, that is, Ga adatom on N-terminating surface and N adatom on Ga-terminating surface.

The problems of the small time-steps for velocity Verlet and other algorithms are concluded and the reasons are attributed as follow: When a smaller time-step is applied, the adatom moves slowly while interacting with the substrate atoms. As the distance moved per time-step is relatively small, the adatom tends to shift with the minimum energy positions as it advances towards the substrate atoms and this is also the adatoms fail to stabilize on top of the substrate atoms when small time-steps are used, regardless of the algorithm used.

To examine the cause of failure when larger time-step sizes are used, an in-depth understanding of the characteristics of the algorithms is essential. For Gear's predictor-corrector, it is often advisable to avoid large-time-steps. The underlying reason is that there is a 'memory effect' especially for the higher order Gear's algorithm. This 'memory effect' will affect the adatoms' subsequent motion as it reduces the effect of the forces experienced at the current positions. As for the r-RESPA, particle-split RESPA is used and different time-steps are applied for the Ga and N adatoms. On the outlook, the different advancement in motion is intended to eliminate the possible problems associate with disparate masses and thus velocities and

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accelerations. However, for the deposition problem, this seems to worsen the situation with the motion of one type of adatoms affecting the other. Hence, the velocity Verlet algorithm seems to be the most suitable and stable among the tested algorithms, as it seems to be able to avoid the problems associated with the Gear's predictor-corrector and r-RESPA.

Other conclusions obtained from the PES are that the energy minimum positions with respect to Ga adatoms are very similar to those reported *ab initio* results in literature [83, 105]. This is probably not surprising as GaN(0001) surface is usually reported to stabilize with a Ga bilayer, behaving like bulk Ga. Since the Ga-Ga interaction modified by Bere *et al.* [90] is with respect to Ga dimers, such reflection of the characteristics of this Ga bilayer can be expected.

Testing of different time-steps using velocity Verlet.

The velocity Verlet algorithm is then tested at different time-step sizes to check for time to reach equilibrium. At small time-step sizes ($\sim 0.001 \tau$ to 0.05τ), longer time to equilibrium is necessary. However, at a much larger time-step ($\sim 0.18 \tau$), the adatoms are moving too fast at each interval such that some adatoms are reflected from the surface. From these results, the time-step selected for the deposition analysis is taken to be 0.1τ . A larger time-step is not advisable for application so as to allow some leeway for the adatoms to react with their environment sufficiently slowly.

5.2 Impact Test

The purpose of this test is to check if sufficient substrate atomic layers are used to ensure the effect experienced by the bottom-most fixed atoms are minimal. In this test, the substrate atoms with exception to the bottom-most 2 layers are allowed to move. The energy of the most bottom unconstrained atomic layer is computed to note for changes especially during the impact with the adatoms. A comparison is made with the energy of an unconstrained layer with no adatoms deposited. This is to simulate the case of an infinitely large substrate in the z-direction. The simulation setup is shown as follows:

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Fig 5.2a: Impact Test simulation setup

The algorithm used in the tests is the velocity Verlet algorithm. The maximum time-step size of 0.1τ obtained from previous test is applied. Prior to the impact test, the substrate atoms are given a small initial velocities. For clearer observations of the influence of atomic deposition with varying the substrate thickness, the temperature control via velocity scaling are not applied.

Fig 5.2b: Combination of results for different substrate thickness

Fig 5.2c: Result for substrate = 5 atomic layers

Fig 5.2e: Result for substrate = 7 atomic layers

Fig 5.2d: Result for substrate = 6 atomic layers

Fig 5.2f: Result for substrate = 8 atomic layers

Fig 5.2g: Result for substrate = 9 atomic layers

Fig 5.2i: Result for substrate = 13 atomic layers

Fig 5.2h: Result for substrate = 10 atomic layers

Fig 5.2j: Result for substrate = 17 atomic layers

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When the substrate is insufficiently thick, the overall system energy will be high and consequently the energy is not fully conserved. This can be seen in **Fig 5.2b** to **Fig 5.2d**, where the equilibrium energy reached is slightly higher than that for the equilibrium energy level for an infinitely thick substrate. However, as the substrate thickness increases, the system can be observed to resemble the infinitely thick substrate behavior. In particular in **Fig 5.2j**, the largest thickness of substrate tested, the energy curve almost matches to that of the substrate of infinite thickness and the impact of the atom deposition is minimal.

Comparing the results, it can be concluded that the least number of atomic layers required to simulate a bulk substrate property is about 10. This would mean that 10 atomic layers = $10 \times x\text{-dimension} \times y\text{-dimension}$ atoms for the substrate alone. The amount of adatoms was about 1 ML (= $2 \times x\text{-dimension} \times y\text{-dimension}$). In other words, the majority of the simulation will be involved in computing the substrate atomic configurations rather than that of the adatoms. Considering the objectives to study the nucleation of the adatoms and the large computational resources required for MD, it was hence proposed that HMC method to be applied for the vapor deposition simulation.

However, as HMC does not allow for a convenient method to compute the simulated physical time, the simulation would focus mainly on interaction trends of the adatoms in the nucleation process. It was important to note that all properties reported would be based on the MD time-step applied at each MC step. The relation to the actual physical time may or may not be the simulated time applied to calculate these properties.

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5.3 Random Number Generation

The random number generator plays a critical role in all stochastic simulation. Although the name implies that the generators will produce numbers randomly (between 0 and 1), in actual case, this is often not true. Hence it was important to check that the randomness of these random number generators prior to actual application and ensure the similarity in results produced by either the Pentium IV PC or the SGI Origin 3000 server used. Since a characteristic of random number generators is that the generated numbers must follow a Poisson distribution (each number have equal probability of being generated), a check on this property was carried out.

Two random number generators were formed and used – *ran()* and *ranf()*. The simulation runs were conducted on the Pentium IV PC and the SGI Origin 3000 server separately and their results were as follow:

PC

Fig 5.3a: Results for *Ranf()* and *Ran()*- PC

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PC

Fig 5.3a(continue): Results for *Ranf()* and *Ran()*- PC

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Server (Origin 3400)

Fig 5.3b: Results for *Ranf()* and *Ran()* – Server

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Fig 5.3b(continue): Results for *Ranf()* and *Ran()*- Server

Fig 5.3c: Comparison of Standard Deviation of *Ranf()* and *Ran()*- PC

Fig 5.3d: Comparison of Standard Deviation of *Ranf()* and *Ran()* – Server

The results shown in Fig 5.3c and Fig 5.3d display similar performance for both PC and server and it is observed that the *ranf()* gives a more uniformly distributed number when the size sampled is >100,000. Understanding these characteristics, for smaller sample sizes ($\leq 100,000$), the *ran()* subroutine was applied due to its relatively lower deviation. For larger sample sizes ($>100,000$), the *ranf()* subroutine was used.

CHAPTER 6

VAPOR DEPOSITION SIMULATIONS

6.1 Simulation Design

The objective of this project is to investigate the effect of strain on QD nucleation from the atomistic approach. To focus on the study of strain-driven diffusion, other diffusion mechanisms are not applied to the simulation. Consequently, a Ga-rich condition is not applied as it will allow for interlayer diffusion of N adatoms within the excess Ga by AELD (Adatom Enhanced layer Diffusion) mechanism [84].

The simulation conditions will be based on the following works [106-108] and the selected parameters are as follow:

- Growth Temperature = $750\text{ }^{\circ}\text{C} = 1023\text{ K}$
- Cell temperature = $914\text{ }^{\circ}\text{C} = 1187\text{ K}$
- Direction of plane grown = $(0\ 0\ 0\ 1) = c\text{-plane}$ or Ga-polarity
- Dimension of substrate = $16 \times 16 \times 1$ lattice units ($x \times y \times z$ -dimensions)
 $\approx 5\text{ nm} \times 5\text{ nm} \times 0.5\text{ nm}$ (PBC applied in the xy -plane)

The width of a small GaN QD is around 5nm and hence for the nucleation, the dimension of the substrate of $5\text{nm} \times 5\text{nm}$ is taken to be sufficient. The smallest possible size is selected mainly due to the computational cost limitation. HMC may be less computation intensive compared to pure MD. However, MD steps are used to propagate the new adatoms' positions for every MC step in the HMC, thus it is still relatively computation intensive.

Prior to the QD growth, simulation is conducted on a commensurate GaN wetting layer strained to the lattice of AlN under the following different III/V ratios:

- N-terminating surface: Ga/N ratio = 1.0
- N-terminating surface: Ga/N ratio = 2.33
- Ga-terminating surface: Ga/N ratio = 1.0

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For the observation of strain-driven diffusion for GaN QD growth, strain variation will be designed into the substrate. The growth conditions simulated are:

- N-terminating, Ga/N ratio = 1.0
- Ga-terminating, Ga/N ratio = 1.0

Although the Ga/N ratios are one of the key influencing factors to the growth, at the initial nucleation stage, the type of terminating surfaces may have an significant influence to this process as the surface atoms are numerous compared to the adatoms. It is important to note that excess Ga is able to stabilise as a metallic bilayer on top of Ga-polarity surface (See *section 3.2* for details). Hence the Ga/N ratio must be sufficiently low to avoid the Ga bilayer formation. Generally, Ga-rich conditions considered in experiments ranged from Ga/N ratio > 4.0 thus the ratio of 2.33 with N-terminating surface is considered suitably low to allow for excess Ga atoms (1 extra Ga adatoms for every Ga-N bond formation) but not high enough for the bilayer to form. However, for the Ga-terminating surface, the Ga/N ratio of 2.33 is sufficient for the Ga bilayer formation and thus this condition is not applied and tested for.

In all simulations, certain degree of simplifications is required under valid and reasonable assumptions. Following are the assumptions made for the simulation:

- GaN and AlN do not undergo evaporation under the conditions applied. The thermal decomposition of GaN exposed to a temperature of 1000 °C and nitrogen pressure of 1 atm is insignificant [110].
- The active nitrogen is taken to be solely the atomic nitrogen. Literature has acknowledged that both atomic nitrogen and N₂ molecules are responsible in the MBE GaN growth [111]. However, for simplification, the nitrogen species are taken to be solely atomic N.
- The simulation is started on the wetting layer which grows commensurately from the AlN pseudo-substrate. The wetting layer is the closest to the AlN and hence is assumed to be under the direct influence of its crystalline order (AlN is more polarized than GaN).
- No adatom is allowed to leave the system once deposited. If an adatom desorbs, a similar adatom will be deposited randomly onto the substrate.

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- No adatom is allowed to diffuse into the substrate. It should be noted that the bond energy of Al-N is much higher than Ga-N such that inter-diffusion is very low. In addition, the simulation starts on the wetting layer of GaN strained to AlN lattice and thus such diffusion is not taken into consideration.

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6.2 Simulation Process

Initialization

- To initialize the coordinates of the wetting layer/substrate atoms
 - options of dimensions of substrate applied, strained/unstrained substrate, N-terminating/Ga-terminating surfaces are allowed
- To set values for the different events

<u>Common</u>	
Number of adatoms per deposition = 36	
Ga/N ratio applied = 1.0, 2.33	
Minimization applied = Conjugate gradient in xyz-directions	
<u>Deposition</u>	<u>Diffusion</u>
<i>no_dt</i> = 300	<i>no_dt</i> = 800
<i>dt</i> = 0.10 τ	<i>dt</i> = 0.05 ~ 0.10 τ
<i>minfrq</i> = 20	<i>minfrq</i> = <i>no_dt</i>

- Compute the neighbour list and the energy of the system

HMC

- Selection of MC event to run (for starting, Deposition event is selected)
- Initialize the momentum (velocities) of the adatoms according to Gaussian distribution at the substrate temperature.
- MD run
 - do (*no_dt*) loops
 - Compute the neighbour list
 - Compute the force and potential of all atoms in system
 - Update the new positions and velocities by Velocity Verlet using *dt*
 - Apply minimization once every *minfrq*
 - Collect the properties (energy, coordinates, order, temperature)
 - enddo
- Compare the energy of the system before and after the MC event and accept the new coordinates by the Metropolis algorithm.
- Repeat Steps 4 to 7 until the desired number of adatoms are deposited.

Fig 6.2a: HMC schematic applied

A schematic of the HMC process applied is shown in Fig 6.2a.

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In MC simulation, the deposition can be taken to be fixed at preset intervals or randomly selected by the deposition probability set. Similarly, the selection of deposition event within the HMC can be taken to be random or fixed. Since the computation method of simulated physical time for HMC is not available, the latter option is applied and the criteria used is the overall acceptance rates. It has been observed that the acceptance rates decrease after a number of MC diffusion events and 45 such events have been found to be satisfactory as the probability of further evolution of the system is almost negligible. Although HMC has been reported to give rise to higher acceptance rates (0.4 to 0.6) than MC methods, it is found that slightly lower acceptance rates of 0.2 to 0.4 is more suitable in this simulation. A lower acceptance rate might indicate a lower computational efficiency but it would also ensure that the system has reached the global minima and hence a lower probability of further evolution.

At the start of each deposition event, the adatoms are randomly distributed at the same atomic height just sufficient for interatomic interaction (1.8σ above the highest atomic position in the system). The atomic types of these adatoms are also randomly set based on the Ga/N ratio set. The depositing adatoms are then given only z -direction velocities according to the cell temperature set towards the substrate. Based on the deposition test conducted (See *section 5.1*), $no_dt = 300$ and $dt = 0.1 \tau$ provide the most suitable configuration for the adatoms to rapidly stabilise onto the surface.

For the start of each MC step, the momentums of the atoms deposited are reset according to the temperature (based on the MD method) by Gaussian distribution. In other words, the velocities of the adatoms are reset in the x -, y - and z -directions. At the end of the MC step, the final coordinates obtained are accepted by the Metropolis criteria.

For simplicity the MD iterations carried out per MC diffusion step is taken to be fixed at 800, which has been tested to be sufficient for the adatoms to obtain a certain level of equilibrium. The integration algorithm used is the velocity Verlet algorithm and the potential applied is the SW potential. Each time-step size, dt , used per MC step is randomly selected within the range of 0.05τ to 0.1τ . This range has

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been tested to provide the highest acceptance rates within the stability range of 0.005τ to 0.15τ applicable to the velocity Verlet algorithm (See *Appendix C* for details).

6.3 Vapour Deposition Simulation Results

The simulation program is written in FORTRAN77 and FORTRAN90. Since the simulation is mainly governed by the random number generating functions and these functions behave similarly using the compilers in the Pentium IV PC or SGI Origin 3000 server as demonstrated in Section 5.3, it is assumed that the results produced are likewise similar. Each simulation run on SGI Origin 3000 server requires approximately 12 to 14 days for completion.

The simulation results shown are some of the selected observations made under the different growth conditions and may not be exclusive to that particular growth condition only.

For ease of comparison and understanding, the definition of the terms used in the subsequent discussions on the analysis and observation of the simulation results are hereby explained:

- *Substrate* is the bulk material where vapour deposition is applied at its surface. Since the wetting layer is applied as the surface to start the deposition, the terms “wetting layer” and “substrate” are inter-changeable hereby.
- *Terminating surface* is defined as the top atomic layer of the substrate prior to the deposition.
- *Nanostructure* is a structure that is at least 1 ML (1 atomic N and 1 atomic Ga layer) high.
- *Island* is a nanostructure.
- *Quantum Dot* is a nanostructure or island formed on strain-varied substrate. (This definition is different from the literature but it is hereby defined so as to prevent confusion with nanostructures, which may be nucleation of thin film rather than quantum dot.)
- *Adatom* is the adsorbed atom on the terminating surface.
- *Adlayer* is a layer of adatoms on the terminating surface.

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- *Excess Ga* is defined as an extended region whereby Ga-Ga interatomic interactions are found.
- *Coverage* is a measure of the number of adatoms deposited.

The description of the positions that can be taken by Ga adatoms are shown:

Fig 6.3a: Sites of Ga adatom (taken from ref. [112])

The description of the positions that can be taken by the single N adatoms are mainly the zincblende and wurtzite position. It had been observed that these are the most frequently pseudo-stable positions taken by these single N adatoms in all the simulation runs. The zincblende position is mainly formed when the single N adatom bonds with 3 other Ga atoms, whereas the wurtzite position forms when the N adatom bonds with only 1 Ga atom. These two positions can be easily distinguished by the height of the N adatom above the Ga layer: the zincblende position is lower than that of the wurtzite position. In addition, the N adatom in the wurtzite position is directly above the Ga atom and not tilted at an angle as in the zincblende position.

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6.3.1 Results: N-terminating surface, Ga/N ratio = 2.33

Fig 6.3.1a: After deposition of 8×36 adatoms (top view)

Fig 6.3.1a(i): After deposition of 8×36 adatoms (side view)

Fig 6.3.1a shows the epitaxial surface after deposition of 8×36 adatoms, just before the next deposition. It can be seen that the N adatoms tend to take position above the first layer of Ga adatoms, which are in either H3 or T4 positions.

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Fig 6.3.1b: After deposition of 13×36 adatoms (top view)

Fig 6.3.1b(i): After deposition of 13×36 adatoms (side view)

Fig 6.3.1b shows the epitaxial surface after the deposition of 13×36 adatoms, just before the next deposition. Compared to **Fig 6.3.1a**, the region whereby the Ga adatoms are in the T4 positions are more widespread in here.

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Fig 6.3.1c: After deposition of 20×36 adatoms (top view)

Fig 6.3.1c(i): After deposition of 20×36 adatoms (side view)

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After the deposition of 20×36 adatoms, it can be clearly seen in **Fig 6.3.1c(i)** that the Ga adatoms form a complete Ga adlayer on top of the N-terminating surface with the adatoms taking the T4 positions. This is intuitively expected as the Ga-terminating surface is more stable than an N-terminating surface for the Ga-polarity GaN. In addition, Ga adatom at T4 position has a slightly lower energy than at the H3 position [105]. The cause for this observation can be related to the effect of the excess Ga adatoms. The deposition of 8×36 adatoms is insufficient for the Ga-adlayer to form and cover the N-terminating surface completely. However, with increasing coverage, the Ga adatoms tend to cover the terminating surface uniformly at the lowest possible energy level, resulting in the surface reconstruction of (1×1) Ga adlayer at T4 positions.

In addition, it can be seen from **Fig 6.3.1c** that excess Ga surround the N adatoms of the nanostructures formed. From the simulation, it is noted that the nanostructures which are surrounded by the excess Ga have lower tendency of changing in shape and size. It appears that the excess Ga plays a role in trapping the N adatoms from desorption or diffusion away from the nanostructures. These excess Ga adatoms at this stage do not necessarily prevent the extension of the nanostructures in terms of its width. One particular observation to support this is shown below in **Fig 6.3.1d** and **Fig 6.3.1e**, for the diffusion process of the N adatom (bordered in red) after the deposition of the 18×36 adatoms. The excess Ga adatoms diffuse slightly away to allow the N adatom to incorporate into the lower atomic layer. This kind of jump is kinetically feasible as the diffusion to such position at the edge is more stable than a higher stand-alone position due to the increase number of bonds formed.

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Fig 6.3.1d: After deposition of 18×36 adatoms (top view)

Fig 6.3.1d(i): (Side view) region bordered in black

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Fig 6.3.1e: After deposition of 19×36 adatoms (top view)

Fig 6.3.1e(i): (Side view) region bordered in black

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Fig 6.3.1f: After deposition of 28×36 adatoms

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However, when the excess Ga region becomes increasing large around the nanostructures, they seem to have an effect of restricting the width of the islands as shown in **Fig 6.3.1f**. This results in the islands' preference of growth by increasing height, with the surrounding excess Ga limiting its width. It is not conclusive if this observation corresponds to actual experimental processes as the inter-diffusion of N adatoms in excess Ga in a Ga-rich environment is not implemented in the present simulation process.

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6.3.2 Results: N-terminating surface, Ga/N ratio = 1.0

Fig 6.3.2a: After deposition of 7×36 adatoms (top view)

Fig 6.3.2b: After deposition of 20×36 adatoms (top view)

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The growth obtained for Ga/N ratio = 1.0 and that for Ga/N ratio = 2.33 are very different. **Fig 6.3.2a** and **Fig 6.3.2b** shows the epitaxial surface after depositing 7×36 adatoms and 20×36 adatoms respectively. The growth of the GaN nanostructure seems to occur only in the regions that are covered by Ga adatoms. Hence it is determined that Ga adatoms are the control species for growth. Compared to the condition of Ga/N ratio = 2.33, the N adatoms have a much larger diffusion time and distance.

In **Fig 6.3.2b**, it can be seen that even after the deposition of 20×36 adatoms, there are insufficient Ga adatoms to form a complete adlayer above the N-terminating surface.

6.3.3 Results: Ga-terminating surface, Ga/N ratio = 1.0

The growth observed seems to be similar to that of Ga/N ratio = 2.33 on N-terminating surface. The excess Ga adatoms are found on the perimeter of the GaN nanostructures. Similarly, at lower coverage, the excess Ga does not hinder the growth of the nanostructures in their width. One such example can be seen in **Fig 6.3.3a** and **Fig 6.3.3b**, where a N adatom (bordered in red) is observed to diffuse to the lower atomic layer in order to fill up a position at a kink.

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Fig 6.3.3a: After deposition of 13×36 adatoms (top view)

Fig 6.3.3b: After deposition of 14×36 adatoms (top view)

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6.3.4 Comparison of Growth Results

Despite the slight variation in growth conditions and terminating surfaces used, the growths obtained are different. A comparison is made by observation of the epitaxial surface after deposition of 20×36 adatoms.

Fig 6.3.4a: Ga/N ratio = 2.33, N-terminating surface. After deposition of 20×36 adatoms

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Fig 6.3.4b: Surface topology of Fig 6.3.4a

After the deposition of 20×36 adatoms under Ga/N ratio = 2.33 conditions on N-terminating surface, the nanostructures formed are relatively flat as shown in **Fig 6.3.4a** and **Fig 6.3.4b**. It is important to note that the surface topology is calculated relative to the terminating substrate surface. Without the consideration of the Ga accumulation, the average island height is approximately 1 ML high from the N-terminating surface.

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Fig 6.3.4c: Ga/N ratio = 1.0, N-terminating surface. After deposition of 20×36 adatoms

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Fig 6.3.4d: Surface topology of Fig 6.3.4c

The growth under Ga/N ratio = 1.0 on N-terminating surface can be seen in **Fig 6.3.4c** and **Fig 6.3.4d** that the distinct islands are formed. In addition, these islands are not surrounded by excess Ga. The average island height is approximately 3 ML high from the N-terminating surface.

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Fig 6.3.4e: Ga/N ratio = 1.0, Ga-terminating surface. After deposition of 20x36 adatoms

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Fig 6.3.4f: Surface topology of Fig 6.3.4e

The growth under Ga/N ratio = 1.0 on Ga-terminating surface in **Fig 6.3.4e** and **Fig 6.3.4f** are quite similar with the growth under Ga/N ratio = 2.33 on N-terminating surface shown in **Fig 6.3.4a** and **Fig 6.3.4b**. The nanostructures are relatively flat and are generally surrounded by excess Ga. The average island height is approximately 2ML high from the Ga-terminating surface.

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6.3.5 Results: N-terminating Strain-varied Surface, Ga/N ratio = 1.0

Fig 6.3.5a: Strain variation applied to Substrate

Fig 6.3.5 shows the strain variation applied to the N-terminating surface. The strain between AlN and GaN is 2% and hence the value of δ applied is 0.02. The shaded regions are marked GaN or AlN, showing the regions that are expected to be the most strained with reference to the labelled material. However, it is noted that the substrate is a wurtzite structure and not a zincblende. Thus, the marked regions are simply a guidance to the estimated strain.

The simulated growth on the strain-varied substrate obtained after deposition of (5×36) , (10×36) , (15×36) and (20×36) adatoms are shown:

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Fig 6.3.5b: After deposition of 5×36 adatoms (top view: left, side view: right)

Initially, the N adatoms are observe to diffuse along the surface until it reaches a region covered with Ga adatoms. However, this does not mean that the N adatoms are trapped at those locations, only that their diffusivity are reduced.

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Fig 6.3.5c: After deposition of 10×36 adatoms (top view: left, side view: right)

The N adatoms are seen to collect around the region of lower strain, though they are still restricted to areas covered by Ga adatoms.

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Fig 6.3.5d: After deposition of 15×36 adatoms (top view: left, side view: right)
Nanostructures are seen to start forming in regions of lower strain.

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Fig 6.3.5e: After deposition of 20×36 adatoms (top view: left, side view: right)

Although nanostructures are increasing in size, they are mainly increased in their width and not height. This is attributed to the strain-driven diffusion of the adatoms to move to regions of lower strain on the substrate surface rather than on top of the islands.

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Compared the epitaxy obtained for an unstrained substrate shown in Fig 6.3.4b, the strain-varied substrate appears to give a much smoother growth that resembles the epitaxy under Ga/N ratio = 2.33 condition on N-terminating surface. For ease of visualization, Fig 6.3.2b is shown hereby in the same orientation as that for Fig 6.3.5e:

Fig 6.3.5f: Repeated Fig 6.3.2b in similar orientation as Fig 6.3.5d

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Fig 6.3.5g: Surface topology for Fig 6.3.5e

Fig 6.3.5h: Surface topology for Fig 6.3.5f

For ease of comparison, the surface topology obtained for **Fig 6.3.5e** and **Fig 6.3.5f** are shown in **Fig 6.3.5g** and **Fig 6.3.5h** respectively. It is to be noted that the surface height is calculated with reference to the substrate surface atoms.

The growth shown in **Fig 6.3.5e** and in **Fig 6.3.5g** is less distinct compared to that in **Fig 6.3.5f** and in **Fig 6.3.5h**. It is believed that the strain variation on the substrate allows for a greater degree of diffusion of the adatoms along the surface and

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hence the smoother growth. The effect of the strain can be seen in that the growth rate at certain parts of the strain varied substrate is slight higher than other regions.

As for the unstrained substrate, the growth is by a kinetic process by which the larger islands will attract more adatoms to themselves. Since there is no strain variation on the substrate surface, the adatoms prefer locations on top of the nanostructures due to the lower energy and thus these islands increase in their heights rather than width.

However, similar to both, the criteria for initiation of growth is the existence of a Ga adlayer above the N-terminating surface.

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6.3.6 Results: Ga-terminating Strain-varied Surface, Ga/N ratio = 1.0

The strain variation and growth conditions applied to the Ga-terminating surface is similar to that of the strain-varied N-terminating surface as shown in **Fig 6.3.5**. The results are presented for the epitaxy observed after the deposition of (5×36) , (10×36) , (15×36) and (20×36) adatoms:

Fig 6.3.6a: After deposition of 5×36 adatoms (top view: left, side view: right)

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Higher diffusivity of the adatoms are observed whereby the general diffusion directions are towards regions of lower lateral lattice distortion (regions which are strained closer to the AlN or GaN).

Fig 6.3.6b: After deposition of 10×36 adatoms (top view: left, side view: right)

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Nanostructures are seen to form at this stage with the Ga adatoms at the perimeter.

Fig 6.3.6c: After deposition of 15×36 adatoms (top view: left, side view: right)

The nanostructures formed at the regions of lower strain are seen to increase in size – height and width.

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Fig 6.3.6d: After deposition of 20×36 adatoms (top view: left, side view: right)

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Fig 6.3.6e: Surface Topology for Fig 6.3.6d

With comparison with the epitaxy on N-terminating surface in Fig 6.3.5d and Fig 6.3.5e and the similar growth conditions but on unstrained substrate in Fig 6.3.4c, the epitaxy on Ga-terminating surface gives rise to a clearer view of the QD nucleation

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regions. It is observed that the expected regions of growth is slightly offset due to possible positions of H3 and T4 that can be taken by the Ga adatoms.

6.3.7 Different Strain Variation

For the purpose of understanding how strain variation might influence the nucleation position, another set of corresponding simulations to those performed in Sections 6.3.5 and 6.3.6 are conducted, but a using different strain profile of the substrate. The strain variation profile applied to these simulations are shown in Fig 6.3.7a:

Fig 6.3.7a: Strain variation applied to substrate

The δ applied is -0.02, similar to that applied in Section 6.3.5, except that the same value is applied to both the x - and y -directions. It is expected that the central part of the substrate has the greatest strain variation and hence highest stress level.

The epitaxy of N-terminating surface and Ga-terminating surface obtained after the deposition of the 20×36 adatoms at the Ga/N ratio = 1.0 are shown respectively:

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Fig 6.3.7b: After deposition of 20×36 adatoms, N-terminating strain varied surface ($\delta_x = \delta_y = 1.0$), Ga/N ratio = 1.0

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Fig 6.3.7c: After deposition of 20×36 adatoms, Ga-terminating strain varied surface ($\delta_x = \delta_y = 1.0$), Ga/N ratio = 1.0

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Fig 6.3.7d: Surface topology of Fig 6.3.7b

Fig 6.3.7e: Surface topology of Fig 6.3.7c

Although the effect of the strain is not clearly seen for the N-terminating surface in **Fig 6.3.7d**, the influence can be observed for the Ga-terminating surface in **Fig 6.3.7e**. The nanostructures obtained are clearly higher at the corners of the substrate than in the central region which is highly strained. From the simulation results, it has been demonstrated that the deposition on N-terminating surface may have involved additional factors which can influence the nucleation positions. As for the Ga-terminating surface, the simulated QDs have shown a preference in nucleating at the predicted regions of lower strain.

CHAPTER 7

DISCUSSION

7.1 Observations and Analysis of Simulation Results

From the simulation results, there are a few similarities for both uniformly and varied strained substrates:

Firstly, the Ga-terminating surface is the most stable terminating surface for Ga-polarity. This can be seen particularly from the growth results on N-terminating surface under Ga/N ratio = 2.33, **Fig 6.3.1a** to **Fig 6.3.1c**. At the starting of the simulation, the Ga adatoms on the surface collect only in certain regions. However, with increasing adatoms being deposited, the excess Ga began to cover the surface and shifting even the nanostructures such that an adlayer of Ga is actually formed directly on top of the N-terminating GaN wetting layer. This shift is uniquely interesting in that it began from a certain region and slowly spread to the whole surface, despite the existing islands formed earlier. In addition, the final positions of these Ga adatoms are T4, which is the lower energy position compared to H3. It is attributed that the shift is made possible due to the relatively small size of these nanostructures. Although such observation has not been reported in the literature and may not even be relevant to the actual process, the result proves that Ga-terminating surface is more energetically stable compared to N-terminating surface for Ga-polarity.

Secondly, the energies of GaN in wurtzite and zincblende structures are the most similar among the III-Nitride semiconductor [113]. It has been suggested from *ab initio* results that the single N adatoms may prefer a zincblende site due to the lower energy levels compared to that of the wurtzite site. This seems to mark true in all the simulation results. Single N adatoms usually stabilize in zincblende position upon deposition. However, these adatoms seem to experience almost similar degree of vibration and diffusivity compared to those in wurtzite positions. Generally, when there are sufficient adatoms (both Ga and N) within interaction range for the formation of a GaN nanostructure, these adatoms will tend to ultimately stabilize into the wurtzite structure which has an overall lower energy level.

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For all the simulations, it is noted that the fault in stacking is usually found in the Ga layer. This is consistent with *ab initio* results reported by Nakamura *et al.* [105], in which they have noted the similar energies of Ga at both the T4 (wurtzite) and H3 (zincblende) position from N-terminating surface at similar heights. This can be seen in the PES – Ga adatom on N-terminating surface at $Z = 1.10$ and $Z = 1.0$ in **Fig 5.1b(vii)** and **Fig 5.1b(viii)**.

Next, it is observed that the growth rate of islands with similar stacking on the top layer is higher than those with different stacking. For example, if all the Ga adatoms are at H3 positions for a particular atomic layer in an island, it will grow much faster compared to another island with Ga adatoms at H3 and T4 positions in an atomic layer. The reason for this is that the atomic layer will tend to vibrate more due to the difference in stacking, causing any adatoms on top of it to diffuse faster rather than stabilizing as the next atomic layer. Consequently, a slower growth results.

In the growth conditions which have more Ga atoms, it is often observed that the excess Ga adatoms surrounded the nanostructures forms and plays the role of reducing vibration and diffusion of the N adatoms. In addition, it is noted that the N adatoms would only stabilize as an adlayer when there are Ga adatoms on top. This is similar to the results reported by Wang *et al.* [94] in their MC work. Another observation is that excess Ga adatoms surrounding the nanostructure may be shifted out if an N adatom approaches as shown in **Fig 6.3.1d** and **Fig 6.3.1e**. However, when the excess Ga adatoms cluster, such a phenomenon is not observed. This may be due to the exclusion of the inter-diffusion of N adatom in excess Ga in the simulation that such occurrence is not observed. It is suspected that the excess Ga has an additional role in the trapping of N adatoms from desorption as remarked by Brown *et al.* in their experimental observations [67].

Although the Ga/N ratios applied here are not strictly Ga-rich when considered experimentally, as the surface atoms are numerous compared to the adatoms during the initial deposition, the effect of excess Ga acting as auto-surfactant is observed. The epitaxy of Ga/N ratio = 1.0 on Ga-terminating surface is found to be very similar to that obtained at Ga/N ratio = 2.33 on N-terminating surface. For both the simulations,

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the resulting epitaxy are relatively smoother compared to the results obtained under Ga/N ratio = 1.0 on N-terminating surface. (Refer to *Section 6.3.4* for details).

Fig 7.1a: Different energy levels resulted from strain

For the strain-varied substrates, the effect of strain from an atomistic viewpoint is studied. Strain in the continuum approach is the atomic displacement across a region. However, at the atomistic level, strain exists in terms of atomic bonds – bond angles and equilibrium bond length. When there is non-uniform strain, the in-plane substrate lattice is distorted and the bond angle is therefore not in equilibrium. This bond angle distortion will cause regions of higher and lower energies as shown in **Fig 7.1a**. Hence, base on the kinetic theories, the atoms will tend to diffuse away from a strained position faster, due to the higher energy, to a position of lower energy, which is closer to the equilibrium. As more adatoms are collected within the lower strain region, the tendency to nucleate as an island is higher. However, this is a simplistic model suitable for elemental epitaxy, such as Si and Ge, and may apply to certain compounds which elements behave similarly to strain.

For GaN however, the situation is made complicated by the different behaviours of Ga and N adatoms under different conditions. As observed for the different strain variations designed into the substrates, the results using N-terminating surfaces appear to be consistently under lesser influence of the strain than those formed on the Ga-terminating surfaces (See *Section 6.3.5 – 6.3.7* for details). Although the simulations on N-terminating surface do display certain diffusion preference due to strain, the exact locations for nucleation seem to be more dependent on the availability of the Ga adatoms.

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As for the Ga-terminating surfaces, this condition of Ga coverage is naturally fulfilled initially. Thus, the QD nucleates preferably at regions that are less distorted such as lattices which are closely matched to undistorted GaN or AlN. In actual experiments, the QDs will nucleate at the region closer to the GaN rather than AlN. However, this is not observed here as the applied wetting layer is not relaxed under the strain for all simulations performed. It is foreseen that this relaxation of strain will induce surface curvatures, which might further influence the preferential diffusion direction and hence the nucleation positions.

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7.2 Recommendations for Future Work

In the present simulation techniques, there are a few possible shortcomings:

- The usage of a short-range SW potential without any long-range term applied
- Insufficient random-ness of the random number generators

Although the HMC method is applied, the results obtained are similarly governed by the potential function as in the MD. However, comparatively, the influence of the potential function may not have such a strong influence in the in HMC. The reason is that HMC allows the resetting of the momentum of the atoms at every MC step. This would actually shift the atoms beyond their current positions and hence sample a wider range of possible configurations. For example, the HMC is able to successfully simulate the surface processes despite the usage of only short-range SW potential as shown in **Fig 6.3.1d**, **Fig 6.3.1e**, **Fig 6.3.3a** and **Fig 6.3.3b**. In addition, the strain-driven diffusion has also been noted for the vapour deposition on strain-varied substrate.

As for MD, the shift in position is restricted by the force, which is the gradient of the potential. Undeniably, the potential still affects the results in HMC such as its inability to simulate the physisorption behaviour. To obtain a more holistic picture, a more complete form of the potential, consisting of long-range term, has to be applied.

In general for solid state MD simulations, there are two common long-range potentials applied:

- Lennard-Jones potential,
$$U_{ij} = 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad (7.2.1)$$

where, ε : the potential well depth

σ : the equilibrium bond distance

r_{ij} : atomic distance between atom i and j

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- Coulombic potential,
$$U_{ij} = \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (7.2.2)$$

where, q_i, q_j : atomic charge associate with ion i and j

ϵ_0 : dielectric constant

r_{ij} : atomic distance between ion i and j

Many approaches have been proposed for the modification of the short-range potential. One of the most common method is to append, or direct addition of, the long-range potential directly to an available short-range potential. Although this method is simple and seems to portray the expected properties in some cases, it is doubtful if the method is universal or that the few proven cases might be mere coincidental or special cases. Basically, this form of modification of the potential will affect all the atoms in the system and may have some undesirable effects unintentionally added as shown:

Fig 7.2a: Direct addition of long-range term to potential

In **Fig 7.2a**, the left shows the possible atomic interactions of the atoms in different situations (atom 1 - bulk, 2 - surface and 3 - adatom) and the right depicts the modified potential where the long-range term has been added as a shell shown in shaded region. It can be clearly seen that the modified potential function performs as designed for atom 3, which is in a position just close enough to the surface for van der Waals interaction only. As for atom 2, its van der Waals interaction with neighbouring surface atoms might be acceptable in that it might display surface reconstruction

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behaviour. However, based on this modified potential, atom 2 also experiences van der Waals interaction with the inner substrate atoms and such interaction is deemed doubtful. In addition, due to this additional interaction with the inner surface atoms, the potential of atom 2 might be much higher than intended by the modified potential. Similarly for atom 1, an atom in a bulk material, its van der Waals interactions with its second or third neighbours are questionable.

Due to these uncertainties, the potential should be modified with care. It is advisable to make certain considerations. Firstly, the ability of the short-range potential to model the bonded atoms interaction has to be taken into account. Although the distinction between short-range and long-range regions are made clear in the simulation, in actual case the potential merely evolves from one to the other continuously, and the interactions can occur simultaneously for the atoms. The direct addition of the long-range potential might alter the behaviour of the short-range (potential well depth, curvature, *etc*) and would have a direct impact on the atomic interaction. For example, the thermodynamic behaviour of the atoms is described by the potential well curvature, since the thermal effect is reflected in the form of atomic vibration.

Fig 7.2b: Modification at different atomic distance ($r_1 < r'_1$)

Such effect is shown in **Fig 7.2b** in which a heating is conducted followed by a cooling: on the left, the interaction crosses over to the long-range part of the potential during the process, whereas on the right, the interatomic interaction remains short-range during the cooling. The final simulation results will thus be very different. The potential in **Fig 7.2b(left)** will result in a volume expansion and decrease in overall system energy during the cooling: the final interatomic distance is r_2 and each bond

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has potential U_2 . On the other hand, the potential in **Fig 7.2b(right)** will return to the initial conditions prior to heating.

Other than the effect of the modification towards the short-range term, care has to be taken to consider the influence of the terminating range of the long-range potential, especially if Coulombic potential is applied. The Coulombic potential can be computed by the Ewald summation method or by multi-pole methods. Although the Coulombic potential is proportional to r^{-1} , for a bulk material, it is reduced to the order of -3 or more. Alternatively, the Coulombic potential can be truncated. However, this truncation range has to be selected carefully. If the range selected is too short, the simulated system might be destabilized [114].

In addition, the gradient of the modified potential has to be checked for continuity as this would in turn affect the forces acting on the atoms. Although the final modified potential might appear smooth and continuous, its gradient might not be equally smooth due to the modification by direct addition. A sudden change in the gradient might result in an unstable system and thus the desirable effect might not be achieved. The usage of switch functions (potential switch or force switch) or shift function might be considered to overcome this problem [115]. Another alternative is to apply truncation function or reaction field method to reduce the range of the long-range term. However, for all modifications to the potential, precautions and validation tests have to be made.

Next, the choice of the type of long-range potential function to be included to the existing short-range term has to be considered. In general, Lennard-Jones potential and Coulombic potential are the two most commonly-used long-range terms applied for solid-state MD simulation. Both potentials have been widely studied and it is generally agreed that Lennard-Jones is best suited for the van der Waals' interaction, while the Coulombic potential is most suitable for the ionic interaction. However, it is noted that these potentials model only the more unique cases of atomic interactions – pure covalent and pure ionic. In reality, there are more compounds than pure elements and these compounds are in varying degrees between pure covalent and pure ionic, thus complicating the modelling process.

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In particular for GaN, the issue is more complex. GaN has a relatively high electronegativity and yet this value is insufficient for GaN to be considered as an ionic compound. Although Coulombic potential is applied for polarized or electrostatic interaction, it is not the only potential form developed for modelling such interactions. The Debye potential in another such potential which has been developed for modelling polarization: dipole-dipole, dipole – induced dipole interactions.

$$\bullet \text{ Debye potential, } U_{ij} = - \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \frac{\alpha_i \mu_j^2 + \alpha_j \mu_i^2}{r_{ij}^6} \quad (7.2.3)$$

where, α_i, α_j : polarizability of atom i and j

μ_i, μ_j : dipole moment of atom i and j

Though this potential is not as popular as the Coulombic potential, it may be more suitable for the situation of GaN.

Instead of a direct application of the long-range term to the existing short-range potential, an alternative modelling process was proposed hereby: the long-range term is to be applied only to specific cases – surface atoms and adatoms. In other words, the long-range term is applicable to atoms which have not formed the equilibrium bond order of 4 as expected in GaN as shown in **Fig 7.2c**:

Fig. 7.2c: Proposed interaction for long-range term

There are several advantages to this design. Firstly, the existing short-range potential will not be altered as the long-range term is not applied to any atom with 4 bonds. Secondly, the interactions of surface atoms and bulk atoms are made distinct from one another. Studies have shown that the properties of surface atoms are different

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from those of the bulk atoms, such as the electrostatic field on the surface. In this way, the surface atoms interaction can be modelled separately from the bulk material. Next, certain computational cost can be saved if the long-range term is applicable to some atoms instead of all atoms. Similarly, the short-range potential for adatoms is not required for computation until they are sufficiently close to form at least one bond with the surface atom.

The long-range term suggested for application is the Debye potential. It is also suggested to assign different atomic charges and polarizability to the atoms according to the bonds formed and atomic type. Different atoms will be polarizable to different degrees with different number of bonds formed: for example, the Ga atom has higher polarizability than N atom. By using the Debye potential, such behaviour can be described and made distinctive.

The proposed modifications have their merits as well as disadvantages. Compared to the direct addition of the long-range term, this method requires more information and the parameterization process is more complex. Intense surface studies, such as surface reconstruction, have to be conducted in order to model the long-range term. In addition, the modification increases the complexity: there are more variations of atomic interactions – atom with single, two or three bonds have different behaviour in their interactions with atom of various bond order. Other than modelling difficulties, the programming of such potential would become more complicated, having to distinguish the atoms for their bonds formed.

Another possible disadvantage is that this modification might exceed the basic MD principle of simplicity: the atoms in the system are assumed to be similar and retain their atomic behaviours throughout the simulation. MD has been proved extensively for its ability to model experimental results with simply the potential function relating interatomic distance and potential energy. However, it was noted that most of the MD simulations are related to bulk material and not for vapour deposition or growth simulation. In fact, one major disadvantage is the inability of the potential to model surface reconstruction during thin film growth. Although this approach to modification might be more complicated, it also allows for the inclusion of additional information which is needed for the simulation of surface science.

Chapter 7: Discussion

As HMC is in essence a MC simulation, another possible alternative may be implemented to allow for physisorption without the application of a long-range term in the potential. Instead, the MC scheme can be applied during certain part of the HMC such as in the diffusion events to allow selected adatoms to randomly move out of position or make certain moves at predefined rates. The main purpose for this scheme is to allow the adatoms to make an even wider selection of moves than allowed by the short-range potential function. However, this application method might further complicate the process to compute the simulated physical time, which is one main problem of HMC.

The next possible error to the HMC simulation is the insufficient randomness of the random number generators which might constitute to larger errors than those caused by the incomplete potential function. This error can cause the collection of adatoms at specific positions as well as give erroneous diffusion directions. However, there is a limitation for solving this problem as random number generators are typically random only for an extremely large number of sampling ranging up to thousands or more. Hence alternatives other than the usage of another random number generator have to be looked into.

One suggested solution is to allow for randomness in more aspects of the simulation. For example, the number of adatoms deposited per Deposition Event can also be made random within a predefined range. Similarly, other parameters, such as the number of *no_dt* loops applied for the MD runs and the occurrence of a Deposition Event can be made random. The disadvantage of this solution is that a larger number of trial runs have to be carried out in order to gauge the optimum ranges for each of these parameters.

Chapter 8: Conclusion

CHAPTER 8

CONCLUSION

The objective of this project is to study the nucleation process of QDs via strain-driven diffusion mechanism during vapour deposition by atomistic approach. The work involved the selection of a suitable simulation technique, and MD and HMC methods were proposed for use. For both methods, an interatomic potential function was required to model the interatomic interactions. Among the existing potentials developed for GaN, the SW potential was chosen for its three-body term, which was regarded as necessary for modelling lattice-mismatch strain, and its ability to model the various defects of GaN. However, it was found that the SW potential had not been tested for its thermodynamic properties and a melting simulation was therefore conducted. From the test, the melting temperature generated by the MD method using the SW potential is 2000 K at a pressure of 1 atm.

Next, the selection of the simulation technique was involved and two preliminary tests – deposition test and impact test – were designed and conducted to gauge the possible computational power required for the vapour deposition simulation: MD method is more computational costly. From the results of the two preliminary tests, it was analyzed that at least 10 unconstrained atomic layers are necessary to model the bulk substrate behaviour. Since QD is three-dimensional structure, it is not possible to reduce the dimensional order so as to reduce the computational cost. Hence HMC was selected for use.

The vapour deposition simulation was carried out for the following conditions:

- Ga/N ratio = 2.33 on N-terminating surface
- Ga/N ratio = 1.0 on N-terminating surface
- Ga/N ratio = 1.0 on Ga-terminating surface
- Ga/N ratio = 1.0 on strain-varied N-terminating surface
- Ga/N ratio = 1.0 on strain-varied Ga-terminating surface

Since inter-layer diffusion of the adatoms was not implemented, the testing under Ga-rich condition (Ga/N ratio > 4.0), which allows for AELD, was not carried

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out. From the results using uniformly strained substrate, a rough growth was achieved for N-rich condition (Ga/N ratio = 1.0 on N-terminating surface), while smoother epitaxy was obtained for slightly Ga-rich condition (Ga/N ratio = 1.0 on Ga-terminating surface and Ga/N ratio = 2.33 on N-terminating surface). The simulations show a high dependency on the terminating surface. In addition, it was shown that Ga-terminating surface was more energetically favourable compared to N-terminating surface and would form preferentially if absence. These results are in order with the current experimental observations.

For the results using the strained-varied substrate, nanostructures were found to nucleate at regions with the minimum in-plane lattice distortion. The adatoms were observed to have a greater diffusivity compared to the results on uniformly strained lattice. This increased diffusivity is attributed to the strain variation of the substrate. However, due to this increase in diffusivity, the adatoms were able to cover a greater distance and a smoother growth was achieved compared to uniformly strained substrate.

Although the various expected trends and surface processes were successfully simulated, the accuracy of the results was still limited by the short-range SW potential function. To simulate a larger range of conditions (such as Ga-rich conditions) and for a holistic simulation with physisorption and chemisorption processes, it is necessary to apply a complete potential, one with long-range and short-range effects. It was suggested in this project to include the long-range Debye potential to the available SW potential by a new approach – to consider the long-range term only when the atoms do not have the complete bond order of 4.

From this project, the potential of HMC for vapour deposition simulations can be seen. Despite its various limitations, the simulations can still be carried out successfully to a certain significant extent. Hence, more research efforts are recommended to further refine this simulation technique and investigate the approaches to solve these very interesting problems.

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Appendix

Appendix A – Differentiation and derivation of equations used in the Simulation

SW potential

$$\phi(1, \dots, N) = \sum_i v_1(i) + \sum_{i < j} v_2(i, j) + \sum_{i < j < k} v_3(i, j, k)$$

where, $v_2(r_{ij}) = \mathcal{E}_2(r_{ij} / \sigma)$

$$v_3(r_i, r_j, r_k) = \mathcal{E}_3(r_i / \sigma, r_j / \sigma, r_k / \sigma)$$

$$f_2(r) = \begin{cases} A \left(\frac{B}{r^4} - 1 \right) e^{\frac{1}{(r-a)}} & , r < a \\ 0 & , r \geq a \end{cases}$$

$$f_3(r_i, r_j, r_k) = h(r_{ij}, r_{ik}, \theta_{jik}) + h(r_{ji}, r_{jk}, \theta_{ijk}) + h(r_{ki}, r_{kj}, \theta_{ikj})$$

$$h_1(r_{ij}, r_{ik}, \theta_{kij}) = \lambda \exp[\gamma(r_{ij} - a)^{-1} + \gamma(r_{ik} - a)^{-1}] \times (\cos \theta_{kij} + \frac{1}{3})^2$$

$$h_2(r_{ji}, r_{jk}, \theta_{ijk}) = \lambda \exp[\gamma(r_{ji} - a)^{-1} + \gamma(r_{jk} - a)^{-1}] \times (\cos \theta_{ijk} + \frac{1}{3})^2$$

$$h_3(r_{ki}, r_{kj}, \theta_{jki}) = \lambda \exp[\gamma(r_{ki} - a)^{-1} + \gamma(r_{kj} - a)^{-1}] \times (\cos \theta_{jki} + \frac{1}{3})^2$$

$$r_{ij} = \sqrt{(x_j - x_i)^2 + (y_j - y_i)^2 + (z_j - z_i)^2}$$

$$\vec{r}_{ij} \cdot \vec{r}_{ik} = |\vec{r}_{ij}| |\vec{r}_{ik}| \cos \theta_{kij}$$

$$\Rightarrow \cos \theta_{kij} = \frac{1}{|\vec{r}_{ij}| |\vec{r}_{ik}|} [(x_2 - x_1)(x_3 - x_1) + (y_2 - y_1)(y_3 - y_1) + (z_2 - z_1)(z_3 - z_1)]$$

$$\text{or } \cos \theta_{kij} = \frac{\vec{r}_{ij} \cdot \vec{r}_{ik}}{|\vec{r}_{ij}| |\vec{r}_{ik}|}$$

Differentiation

$$\frac{df_2}{dr_i} = -A \exp[(r - a)^{-1}] \times \left[\frac{4B}{r^5} + \frac{Br^{-4} - 1}{(r - a)^2} \right]$$

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$$\begin{aligned}\frac{dh_1}{dr_i} &= \lambda \exp[\gamma(r_{ij} - a)^{-1} + \gamma(r_{ik} - a)^{-1}] \left[\cos \theta_{jik} + \frac{1}{3} \right] \\ &\times \left\{ 2 \frac{d \cos \theta_{jik}}{dr_i} - \gamma \left(\cos \theta_{jik} + \frac{1}{3} \right) \left[\frac{1}{(r_{ij} - a)^2} \frac{dr_{ij}}{dr_i} + \frac{1}{(r_{ik} - a)^2} \frac{dr_{ik}}{dr_i} \right] \right\} \\ \frac{dh_2}{dr_i} &= \lambda \exp[\gamma(r_{ji} - a)^{-1} + \gamma(r_{jk} - a)^{-1}] \left[\cos \theta_{ijk} + \frac{1}{3} \right] \times \left\{ 2 \frac{d \cos \theta_{ijk}}{dr_i} - \gamma \left(\cos \theta_{ijk} + \frac{1}{3} \right) \times \frac{1}{(r_{ji} - a)^2} \frac{dr_{ji}}{dr_i} \right\}\end{aligned}$$

$$\begin{aligned}\frac{dr_{ij}}{dx_i} &= -\frac{(x_j - x_i)}{r} \\ \frac{dr_{ij}}{dy_i} &= -\frac{(y_j - y_i)}{r} \\ \frac{dr_{ij}}{dz_i} &= -\frac{(z_j - z_i)}{r}\end{aligned}$$

$$\begin{aligned}\frac{d \cos \theta_{213}}{dx_1} &= \frac{2x_1 - x_2 - x_3}{r_{12}r_{13}} + \frac{x_2 - x_1}{r_{12}^2} \cos \theta_{213} + \frac{x_3 - x_1}{r_{13}^2} \cos \theta_{213} \\ \frac{d \cos \theta_{213}}{dx_2} &= \frac{x_3 - x_1}{r_{12}r_{13}} - \frac{x_2 - x_1}{r_{12}^2} \cos \theta_{213} \\ \frac{d \cos \theta_{213}}{dx_3} &= \frac{x_2 - x_1}{r_{12}r_{13}} - \frac{x_3 - x_1}{r_{13}^2} \cos \theta_{213}\end{aligned}$$

or, by dot product,

$$\begin{aligned}\frac{d \cos \theta_{213}}{dx_1} &= \frac{1}{|r_{12}| |r_{13}|} \left[-(x_2 + x_3) + 2x_1 \right] + \frac{\vec{r}_{12} \cdot \vec{r}_{13}}{r_{13}} \times \frac{x_2 - x_1}{r_{12}^3} + \frac{\vec{r}_{12} \cdot \vec{r}_{13}}{r_{12}} \times \frac{x_3 - x_1}{r_{13}^3} \\ \frac{d \cos \theta_{213}}{dx_2} &= \frac{1}{|r_{12}| |r_{13}|} \left[x_3 - x_1 \right] - \frac{\vec{r}_{12} \cdot \vec{r}_{13}}{r_{13}} \times \frac{x_2 - x_1}{r_{12}^3} \\ \frac{d \cos \theta_{213}}{dx_3} &= \frac{1}{|r_{12}| |r_{13}|} \left[x_2 - x_1 \right] - \frac{\vec{r}_{12} \cdot \vec{r}_{13}}{r_{12}} \times \frac{x_3 - x_1}{r_{13}^3}\end{aligned}$$

Note: Both the derivation of cosine, either by dot product or by cosine rule, should give the same final value.

Appendix

Appendix B – Flow chart of Heating and Melting simulation

Appendix

APPENDIX C – Testing of different ranges of dt and dt_no

There are several parameters for the HMC simulations that can be modified and tuned to obtain the desirable acceptance rates. A brief description of each parameters are made:

For MC

- *dep_freq*: the rate at which the next deposition event is carried out. For simplicity, this rate is taken to be fixed. It is examined that the evolution of the simulation is usually within the first 45 MC steps of Diffusion event. The typical acceptance rates in all the simulation range from 0.3 to 0.5.
- *noAdd*: number of adatoms deposited per Deposition Event. This number is taken to be a constant 36 which give rise to an average surface coverage of 14% and is assumed to be sufficiently small to prevent clustering. Although smaller sizes can be applied, the simulation time required will increase.

For MD runs (Diffusion Event)

- *dt*: the time-step size used in the MD. The integrating algorithm applied is the velocity Verlet and its tested range of stability is from 0.002 to 0.12.
- *no_dt*: the number of iterations run for the MD part in HMC. Usually the larger the *no_dt* should give better equilibrium result. However, it is inefficient to use an extremely large value as this will increase the computational time.
- *minfreq*: the frequency at which minimization is applied. It is to be noted that in general the vapour deposition simulations do occur in equilibrium condition. In fact, such MD simulation is taken to be Non-Equilibrium MD (NEMD). A possible effect of applying minimization frequently might be trapping the adatoms in certain positions which would defeat the purpose of the MD run as ‘random-walk’ for the MC step. Thus, minimization is applied only at the end of the MD run and its main role is to ensure that the system has obtained a certain level of equilibrium for its energy and coordinates to be sampled by the Metropolis algorithm.

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For MD runs (Deposition Event), although the involved parameters are similar to that used in the Diffusion Event, different set of values are used. These parameters are taken to be constant as the main purpose of this MC step is assumed to allow new adatoms enter and settle into random positions on the surface since the different surface processes are not considered.

Preliminary deposition tests are carried out with similar conditions as for the vapour deposition simulation and some of the results are shown below:

Fig C.1 – percentage acceptance for different dt ($no_dt = 500$)

Fig C.2 – percentage acceptance for different dt ($no_dt = 800$)

Appendix

Fig C.3 – percentage acceptance for different dt ($no_dt = 800$)

From Fig C.1 and Fig C.2, it can be observed that the percentage acceptance increases with no_dt . A larger range of dt was then selected to run in Fig C.3. It is found that the average percentage acceptance levels from $dt = 0.0625$ to $dt = 0.0925$. This result is believed to be desirable as the acceptance should not be dependent on the values of dt . Hence, the range of dt is taken from 0.05 to 0.10 and no_dt is fixed at 800.